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DEVELOPMENT OF
LITHIUM INORGANIC ELECTROLYTE BATTERIES
FOR NAVY APPLICATIONS

by

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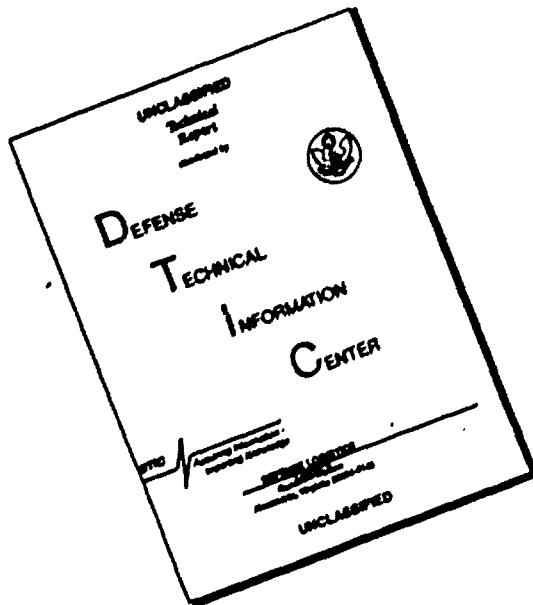
October 1975

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FOREWORD

The purpose of this report is to present pertinent test results, development accomplishments and application experience gained during FY 75 with new lithium-inorganic electrolyte cells (Li + SOCl₂).

This work was sponsored by the Office of Naval Research, Vehicle Technology Department and NUC Independent Exploratory Development program. The exceptional interest and guidance provided by Drs. George Neece (ONR), Rudolph Marcus (ONR), Eugene Cooper (NUC), and Howard Wilcox (NUC) are very much appreciated. Dr. Thomas Lang and Dr. Sachio Yamamoto provided the facilities and direction for this program.

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This report was reviewed and released by

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ABSTRACT

During Fiscal Year 1975 the Naval Undersea Center (NUC) performed an extensive test program with low-rate and high-rate lithium-thionyl chloride (S9C1₂) cells. This program has aided in identifying capabilities and deficiencies with the present technology. Many deficiencies were readily corrected but others are less understood and additional development is required. As a result of this program, improved, low-discharge rate, hermetically sealed cells and batteries are being used in several ocean oriented applications. Future development programs are planned to provide safe, high-discharge rate cells for propulsion and pulse-power applications.

INTRODUCTION

A new lithium-inorganic electrolyte battery is now available that has valuable properties¹²³. It has high-energy density and the potential for a long shelf life; it can be configured for either low or high discharge rates and from very small to very large size cells. These characteristics are valuable to many ocean-oriented applications, including oceanographic instrumentation, sonar systems, biotelemetry devices, undersea weapons, small undersea vehicles, meteorological instrumentation, field communications, etc. However, only limited performance, safety and cost data has been available for this battery, which was insufficient for a complete evaluation and selection for projected ocean-oriented applications.

The objective of this program was to determine the performance, safety, reliability and environmental limits of this battery as configured for ocean systems and to provide basic data for planners and designers of future military ocean systems. The major criteria investigated included energy per weight, volume and cost; power and endurance range; sensitivity to low temperature and depth; storage environments; operability and reliability; deployment factors; and cell emissions and hazards.

This program was implemented by first analyzing numerous possible applications to identify representative testing requirements. Three detailed test plans were prepared: (1) to determine the normal operating parameters to be expected from the cells; (2) to explore cell output characteristics during anticipated Navy use; and (3) to become aware of any possible hazards from mishandling of large batteries made from these cells.

Cells of various sizes and discharge rate designs were procured and tested. The tests identified numerous physical, material, engineering and operational deficiencies. Experiments were initiated to discover ways to overcome these weaknesses. As a result, the corrections accomplished now provide a technology that is being used in multiple applications.

This report describes the types of cells tested, the test program, pertinent test results, cell improvements that have been made, application experience to date and recommended development needed for wide applications of the technology.

CELL DESCRIPTION

At the present time prototype lithium cells, with an inorganic liquid as the electrolyte, are available from several companies including GTE Laboratories, P. R. Mallory & Co. Inc., Honeywell Inc., and Electrochemica Corp. The electrolyte is composed of inorganic salts in an inorganic solvent, and energy is produced by the electrochemical decomposition of the inorganic solvent material at the carbon electrode and oxidation of the lithium during discharge of the cell. The inorganic solvent decomposes only when the load circuit is closed thereby making it possible for the battery to operate effectively for several years.

The inorganic lithium battery has an open circuit voltage of 3.6+ volts. Unlike conventional solid cathodes the distance between the reactive zones of the electrodes remains nearly constant upon discharge and the cells exhibit exceptional voltage stability, approaching 1 percent. Since the electrolytic solution is also the depolarizer, the weight of the cathode does not burden the cell and energy densities of 250 watt-hours/lb to 90% of the initial voltage are realized in simple cells.

Table 1 compares the performance characteristics of various battery systems. Beyond the weight and volume advantages, the lithium inorganic electrolyte cell has cost advantages that make it particularly attractive in large size cells of 100, 1000 or 10,000 ampere hours.

The chemistry of the lithium anode cell is not well defined. The only thing that is not in doubt is the fact that the lithium is being oxidized from the zero to the plus one state and the sulfur is being reduced to either

TABLE I
Comparison of Primary Cells

| <u>SYSTEM</u> | <u>LB/KWH</u> | <u>IN³/KWH</u> | <u>\$/KWH*</u> |
|--|---------------|---------------------------|----------------|
| Alkaline (Zn/MnO ₂) | 33 | 473 | 3.69 |
| Mercury (Zn/HgO) | 22 | 216 | 73.39 |
| Silver/Zinc (Zn/Ag ₂ O) | 17 | 262 | 303.58 |
| Lithium Inorganic (Li/SO ₄ Cl ₂) | 5 | 81 | 2.26 |
| Lithium Organic (Li/SO ₄) | 12 | 203 | 5.27 |

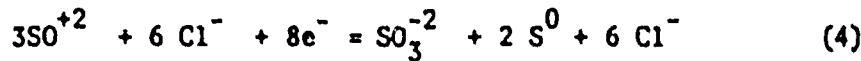
*Cost of active components

to the element or another oxidation state. It is likely that more than one reaction is taking place. The source of the sulfur is thionyl chloride (SOCl_2).

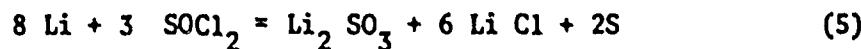
The chemistry of thionyl chloride is interesting. It is capable of dissociating in at least two ways



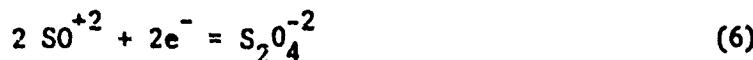
One possible set of half cell reactions is as follows:



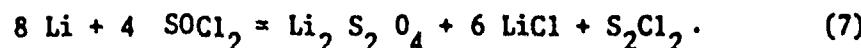
By adding equations (3) and (4) the overall reaction can be described as



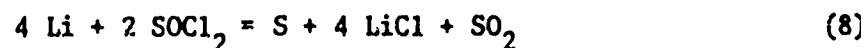
The following half-reaction is also possible



and leads to a second reaction that can be hypothesized,



For completeness there is a third reaction that may be considered, but if it goes at all it is certainly not an important reaction. This reaction is



The absence of a large sulfur dioxide pressure suggests that the reaction is of lesser importance. On disassembly of discharged batteries, large amounts

of elemental sulfur are always seen. This fact suggests that equation (5) is the most important.

Four sizes of cells have been tested, AA, D, Double D, and 100 AH sizes, in this program. Principal design characteristics of these cell types are shown schematically in Figure 1. A simple "bobbin" type of cell construction was preferred for low rate applications. This consisted of a central "bobbin" cathode and a peripheral cylindrical anode attached to the cell container. This cell type was labeled "High Energy Cell" with a maximized capacity obtainable below a certain limiting discharge rate. The second "jelly roll" cell type is the "High Power Cell" shown in the same figure. It comprises high surface area electrodes assembled in a wound configuration for high rate applications. Both cell types are built using commercial cell hardware wherever possible. A hermetic seal was designed specifically for use with the inorganic lithium battery system. A more conventional battery crimp seal was developed and tested. Cells were built with both types of seals using practical assembling procedures.

CROSS SECTION COMPARISON

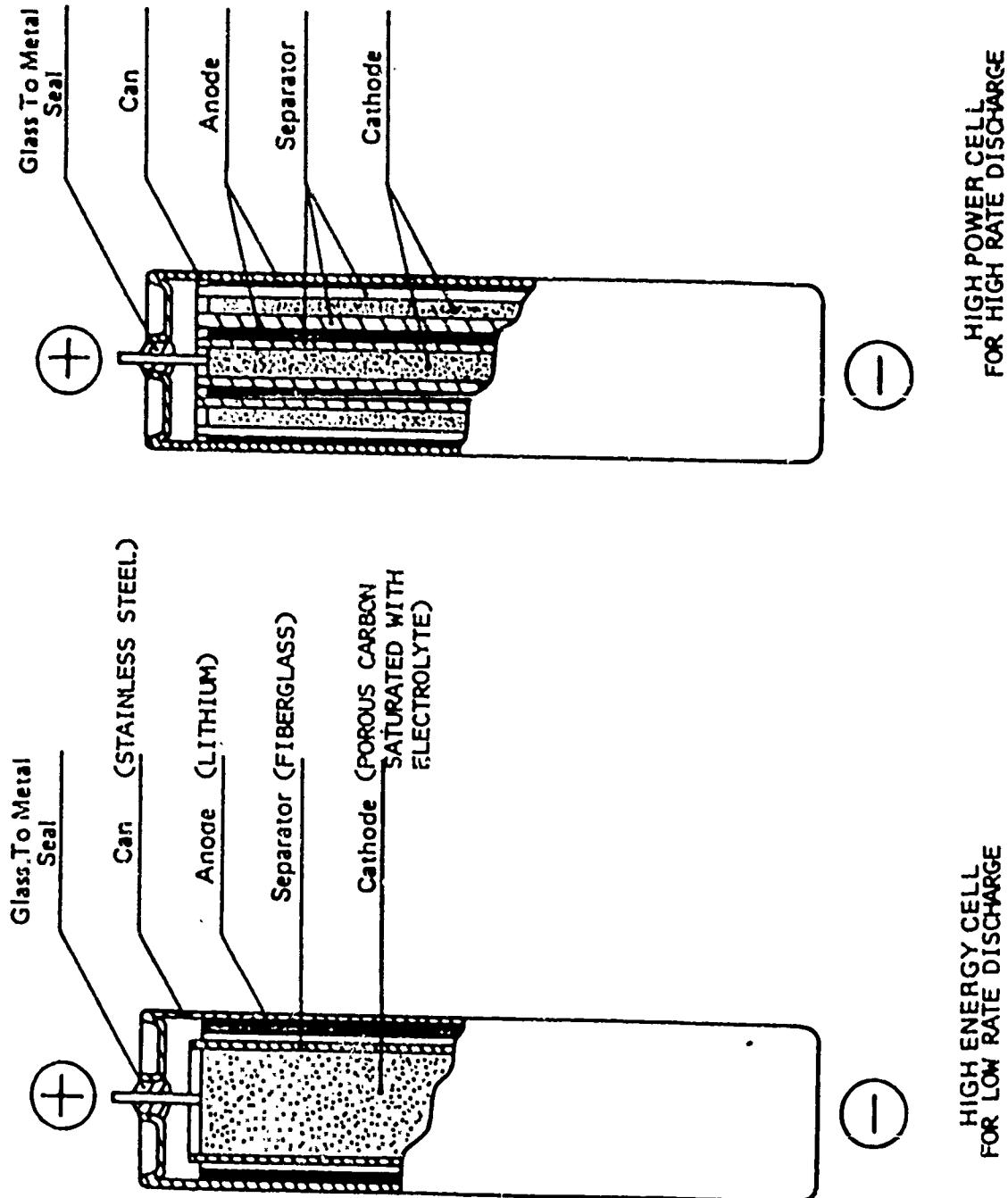


Figure 1. Cross Section Comparison

CELL TEST

Three detailed test plans were prepared: (1) to determine the normal operating parameters to be expected from the Lithium-Inorganic electrolyte cells; (2) to explore cell output characteristics during anticipated Navy use; and (3) to become aware of any possible hazards from mishandling of large batteries made from these cells. These tests are outlined in Table II. The four cell sizes tested are AA, D, DD, and the experimental 100 ampere-hour cell.

Figures 2, 5 and 4 show the D-sized cells upon arrival at the Naval Undersea Center. A poor choice of packaging material was immediately noticed. Cardboard cartons and paper, used to separate the layers of cells, are inadequate packing materials if any electrolyte leaks from a cell since paper is rapidly destroyed by SOCl_2 . Upon closer examination of the individual cells, several were shown to be corroded around the cell seal or had blisters or holes in the epoxy seal. This was the first indication that the crimp sealing technique was inadequate. Ten percent of the cells had some case corrosion around the top seal area.

The weight of these cells varied slightly as shown in Figure 5 but averaged 98.86 grams. The cells voltage was measured to detect faulty or internally shorted cells. Figure 6 shows a histogram of cell voltages and indicates an open circuit voltage of approximately 3.6 volts. Each cell was washed with distilled water and the pH of the wash water was determined to give an indication of the presence of acid on the cell case. Figure 7 presents the approximate pH of the cell cases. The pH of the cell wash water was normally 7 with minimums of 3.9 for 5% of the cells.

TABLE II

TEST PLAN

Low and High Rate Cells

(1 AH, 12 AH, 100 AH & 1000 AH Cells)

| | | |
|-------------|-------------------------------|---|
| INCOMING | Electrical, Mechanical, X-Ray | |
| PERFORMANCE | - w/o storage | |
| | with storage (lab) | Continuous Discharge (low, med & high rates) |
| | with storage (heat) | |
| | with storage (humidity) | Pulse Discharge |
| ENVIRONMENT | - Shock | |
| | Vibration | |
| | Tumbling | |
| | Hydrostatic | |
| | Altitude | |
| SAFETY | - Nail Penetration | |
| | Series Dead Cell | |
| | Parallel Dead Cell | |
| | Drop Cell | |
| | | |

Figure 2. D-Size Cells in Their Shipping Box

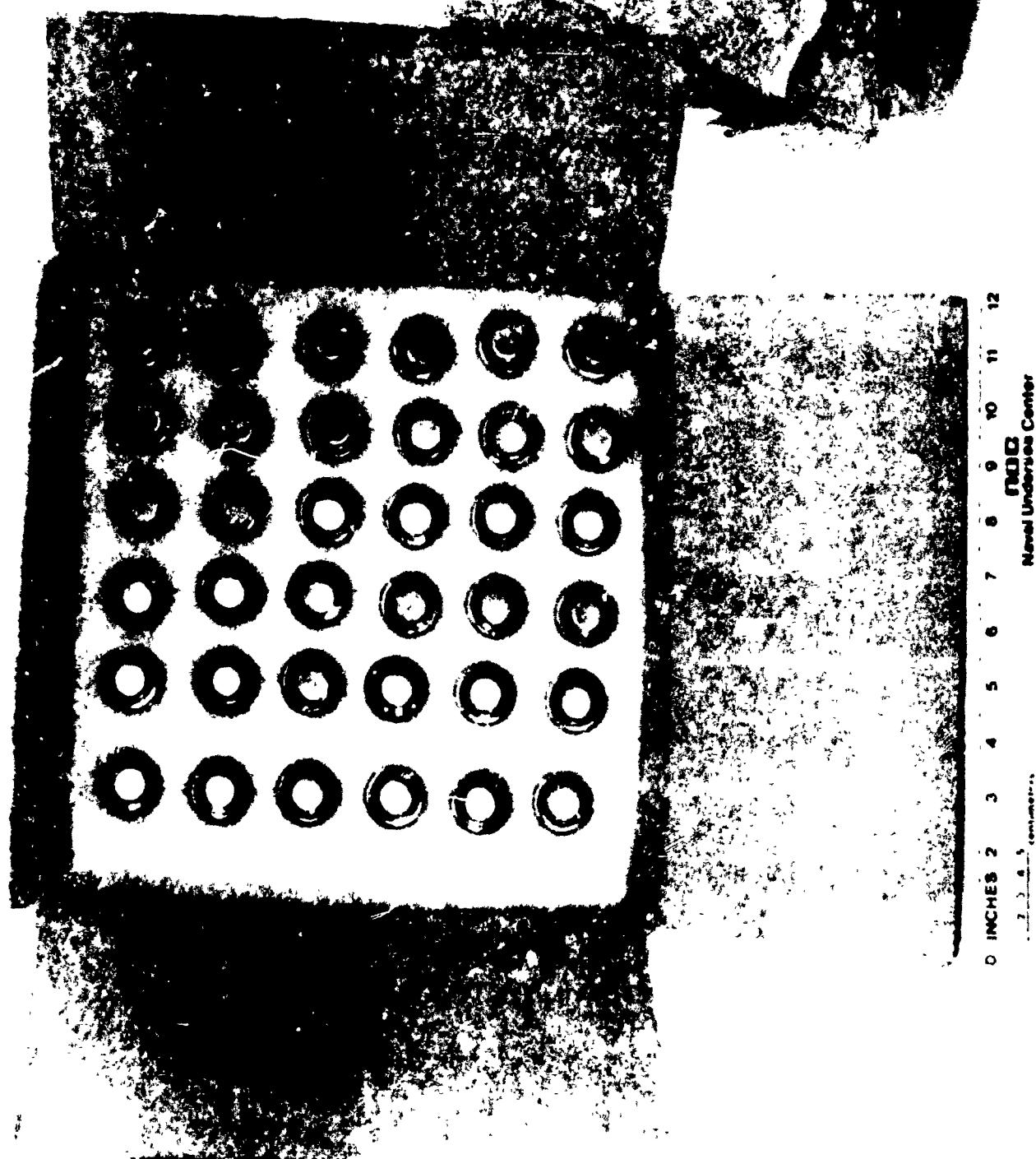
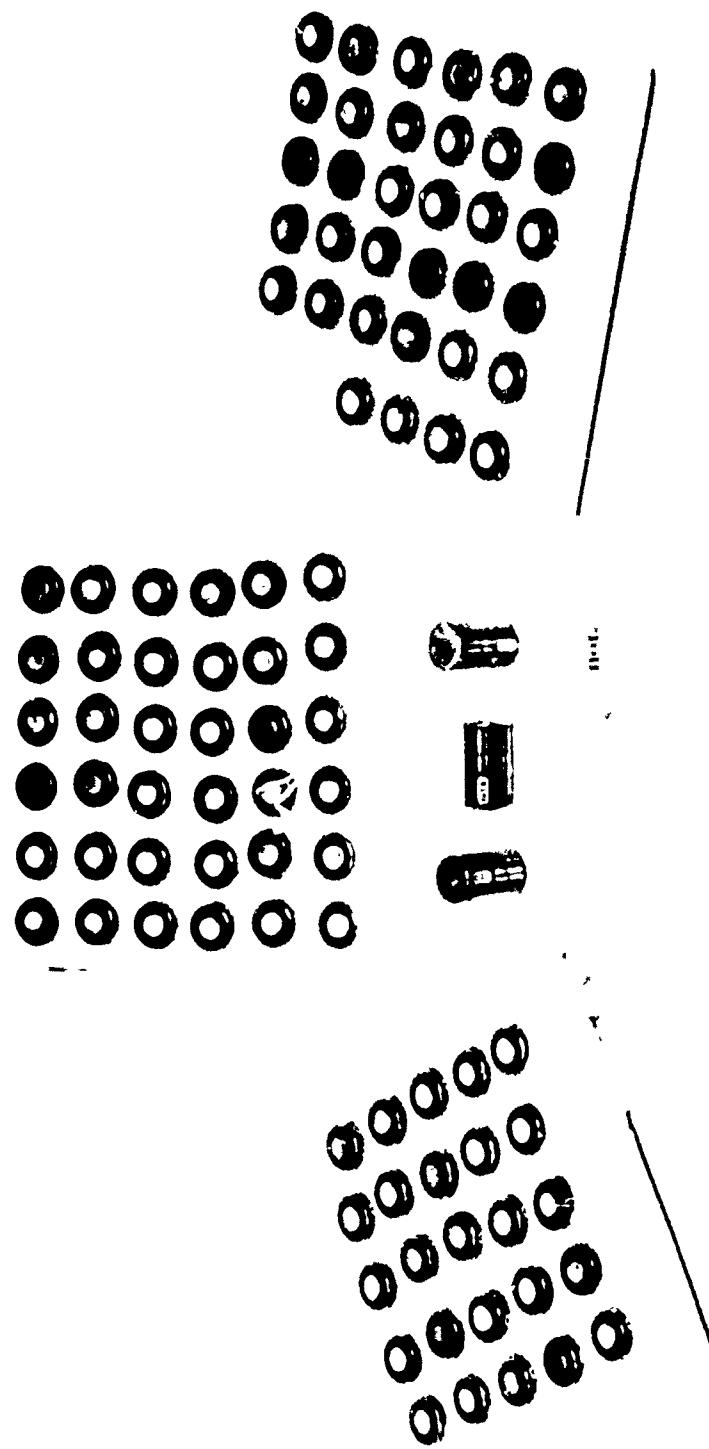


Figure 3. The Three Layers of Cells



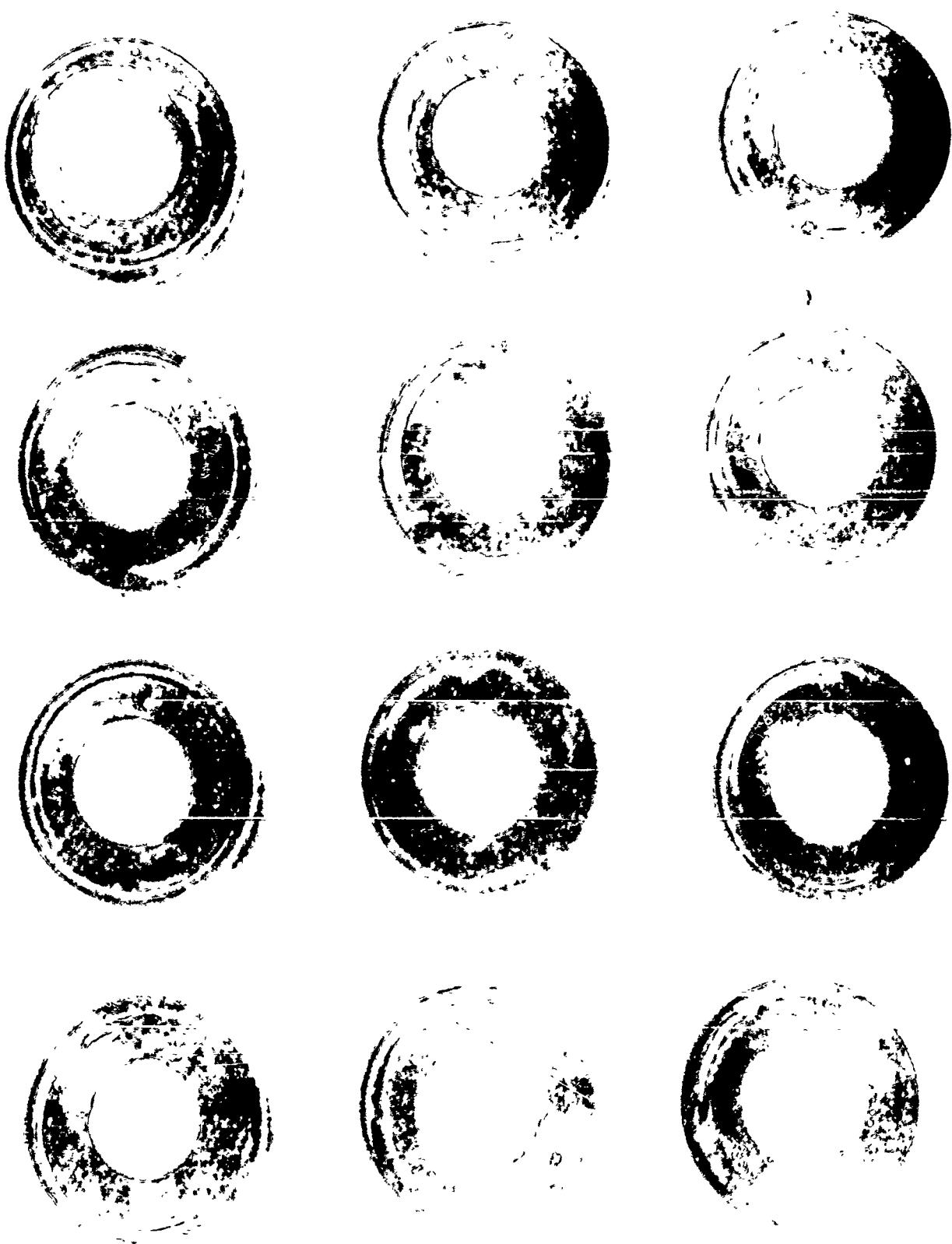


Figure 4. Close Up of Cell Tops Showing Seal Problems

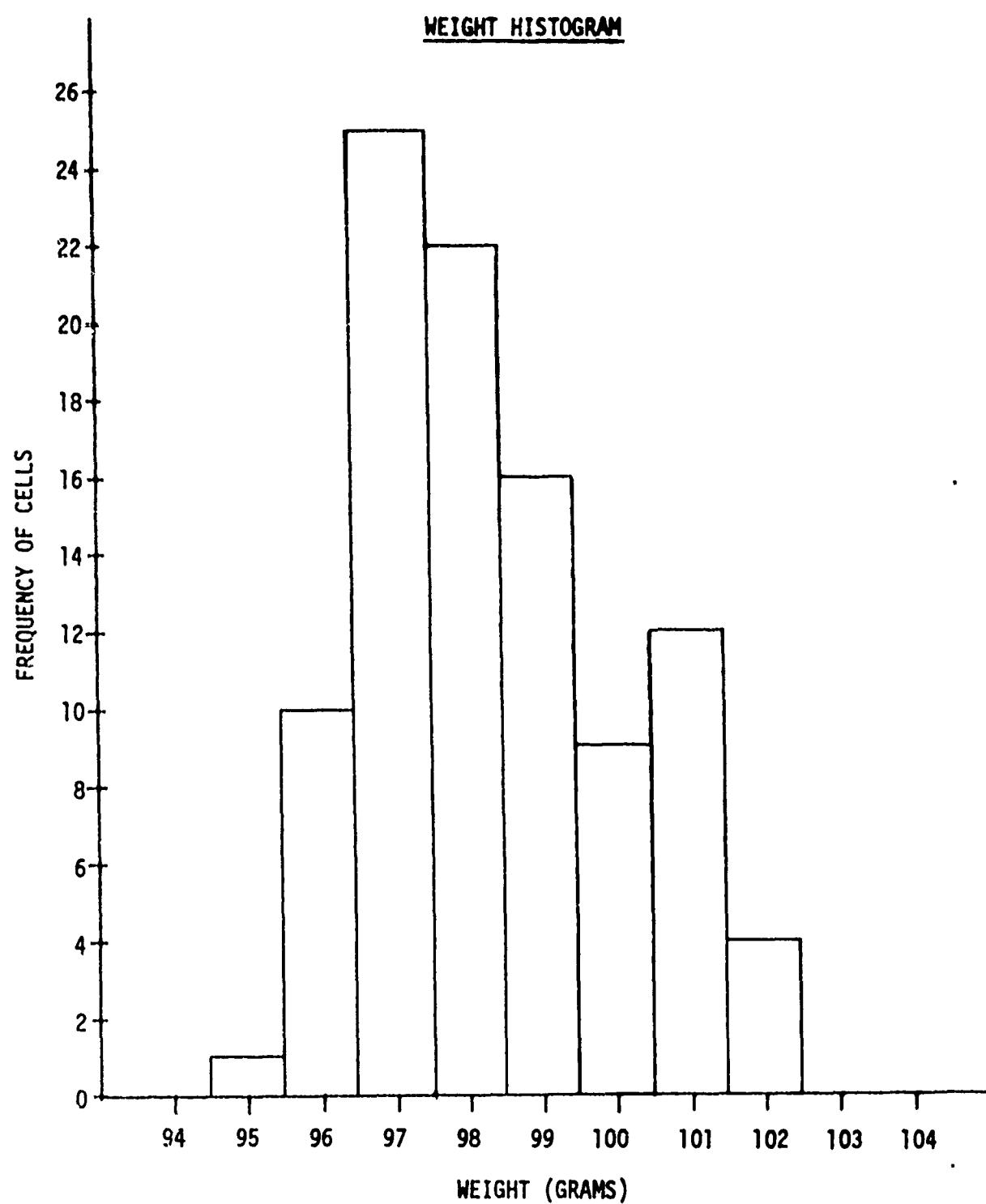


Figure 5. Histogram of Cell Weights

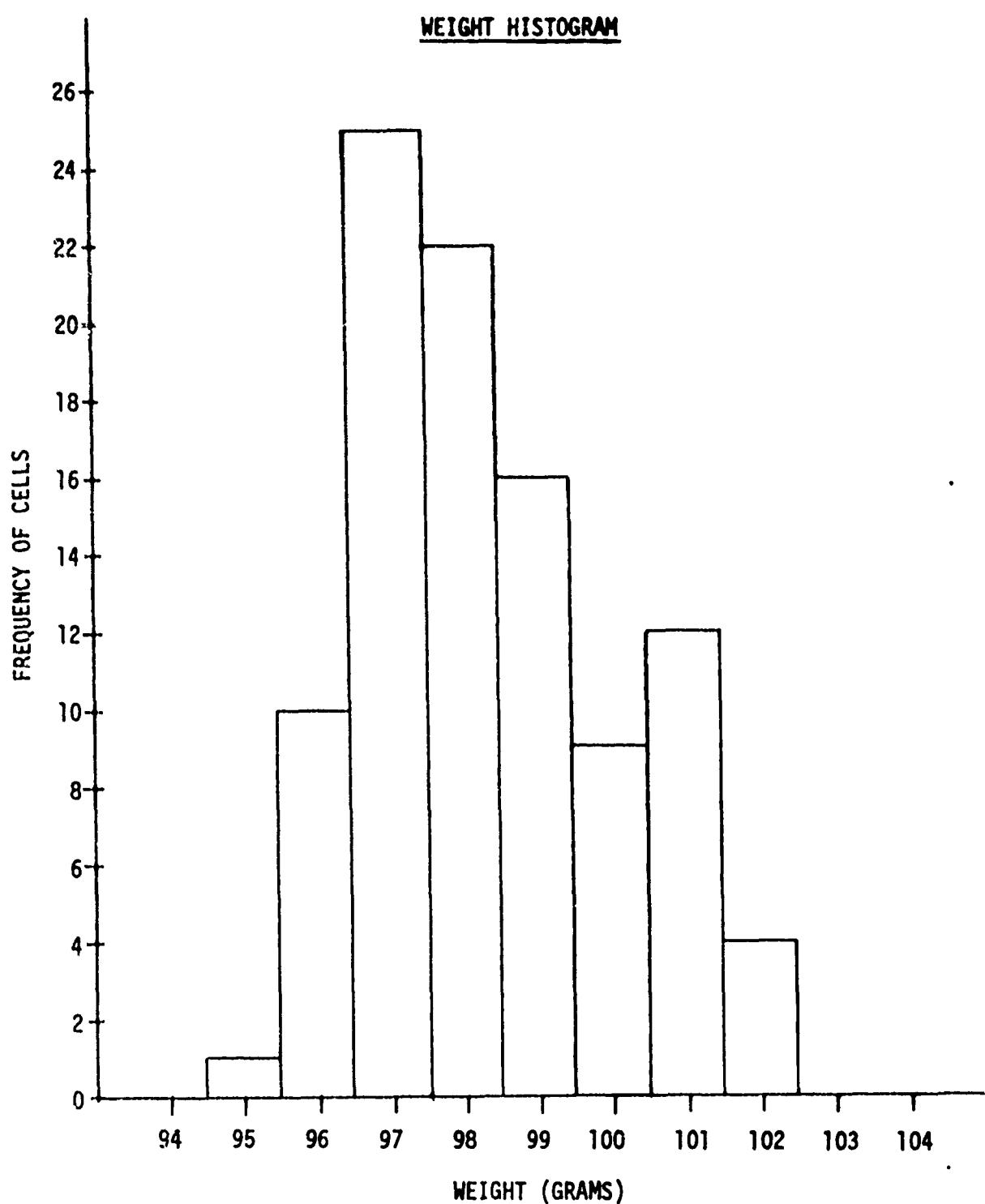


Figure 5. Histogram of Cell Weights

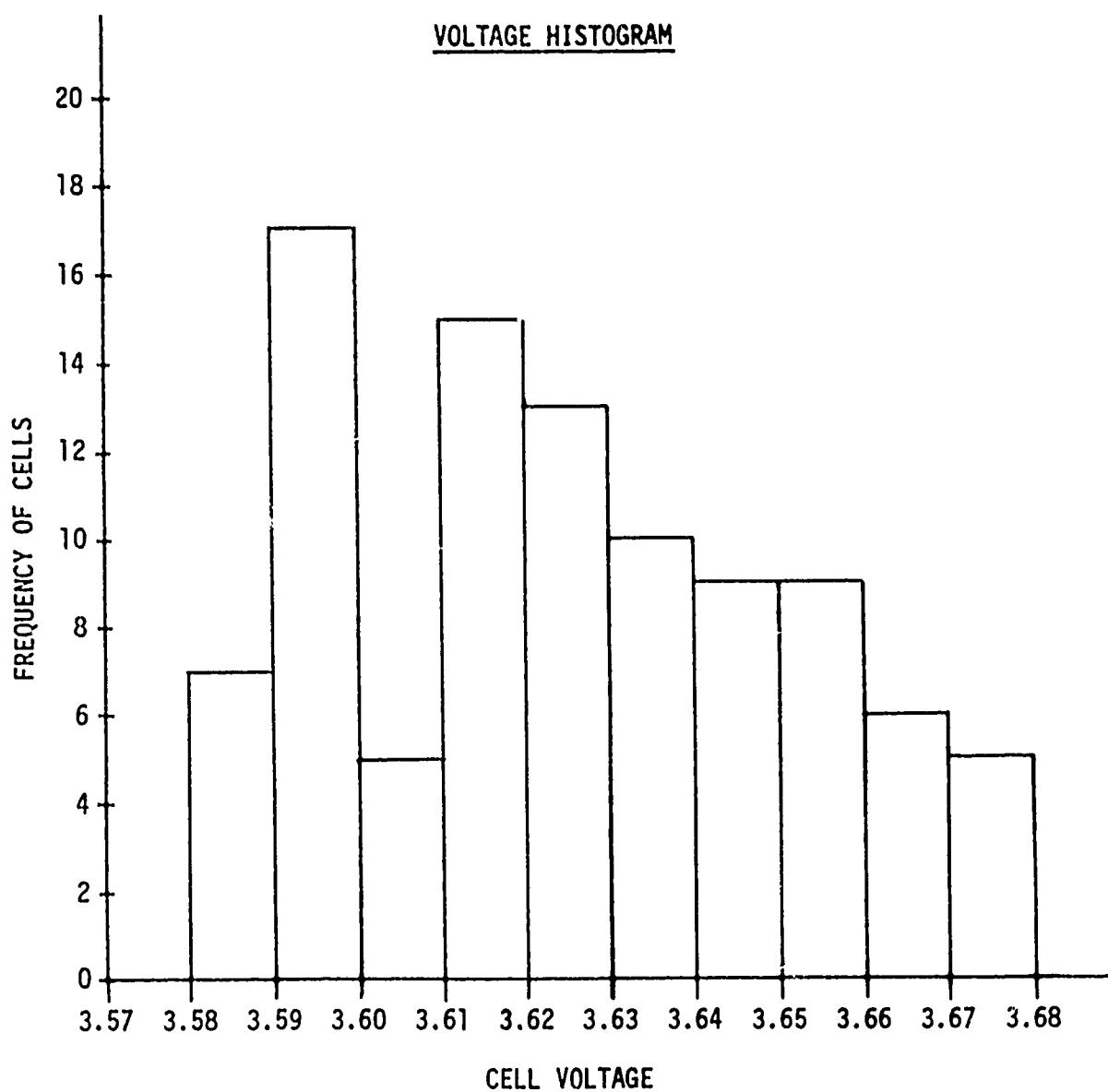


Figure 6. Histogram of Open Circuit Cell Voltages

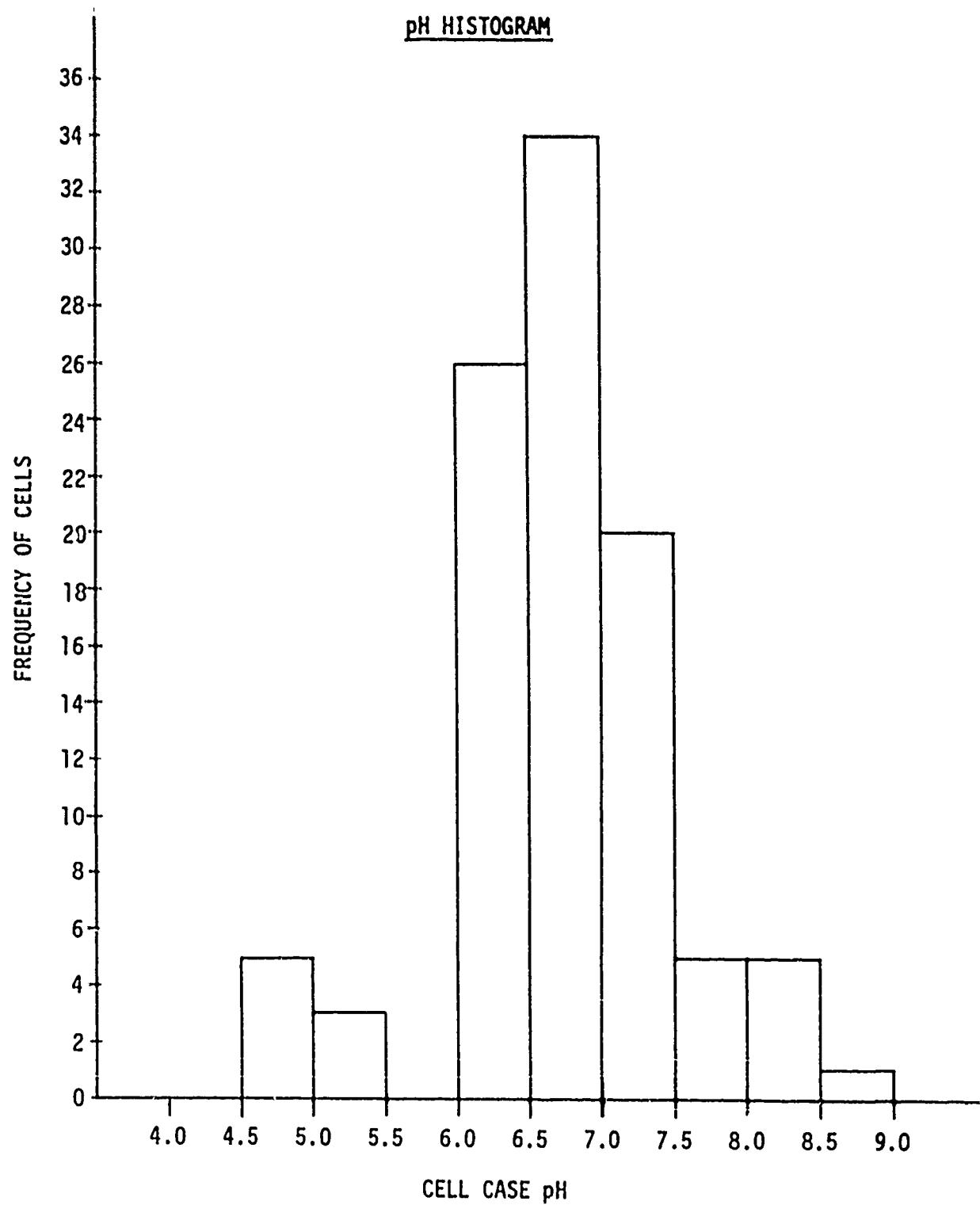


Figure 7. Histogram of Cell Case pH

An X-ray was made of selected cells to show the internal construction. X-raying the batteries in different orientations and at various states of discharge can provide important information. The quantity of remaining electrolyte and the lithium lining the can wall can be determined. The top two cells of Figure 8 are fresh whereas the lower cell is completely discharged. Figure 9 shows both the AA and D-sized cells in a different orientation. In this figure cell #1 is a fresh cell, cell #5 is fully discharged and cell #20 is partially discharged. Observing the thin layer of lithium lining the case wall and the gas above the electrolyte are ways to determine a fresh cell.

Cel

A series of performance tests was conducted to determine the discharge capacity, available ampere-hours and shape of the discharge curve. The cells tested are shown in Figure 10. These batteries were sealed with either the hermetic or the teflon-metal crimp seal. During the tests the batteries were placed either in a refrigerator at 5°C or were maintained at room temperature. Table III summarizes the results from the tests.

Test 1

Three successive tests were conducted on one AA sized hermetically sealed cell. The discharge rates were 1 milliampere, 10 milliamperes, and 100 milliamperes. The battery voltage exhibited good voltage regulation at all discharge rates, although 100 milliamperes is an abnormally high continuous discharge rate for AA size cells.

Figure 8. X-Ray of Three D-Sized Cells

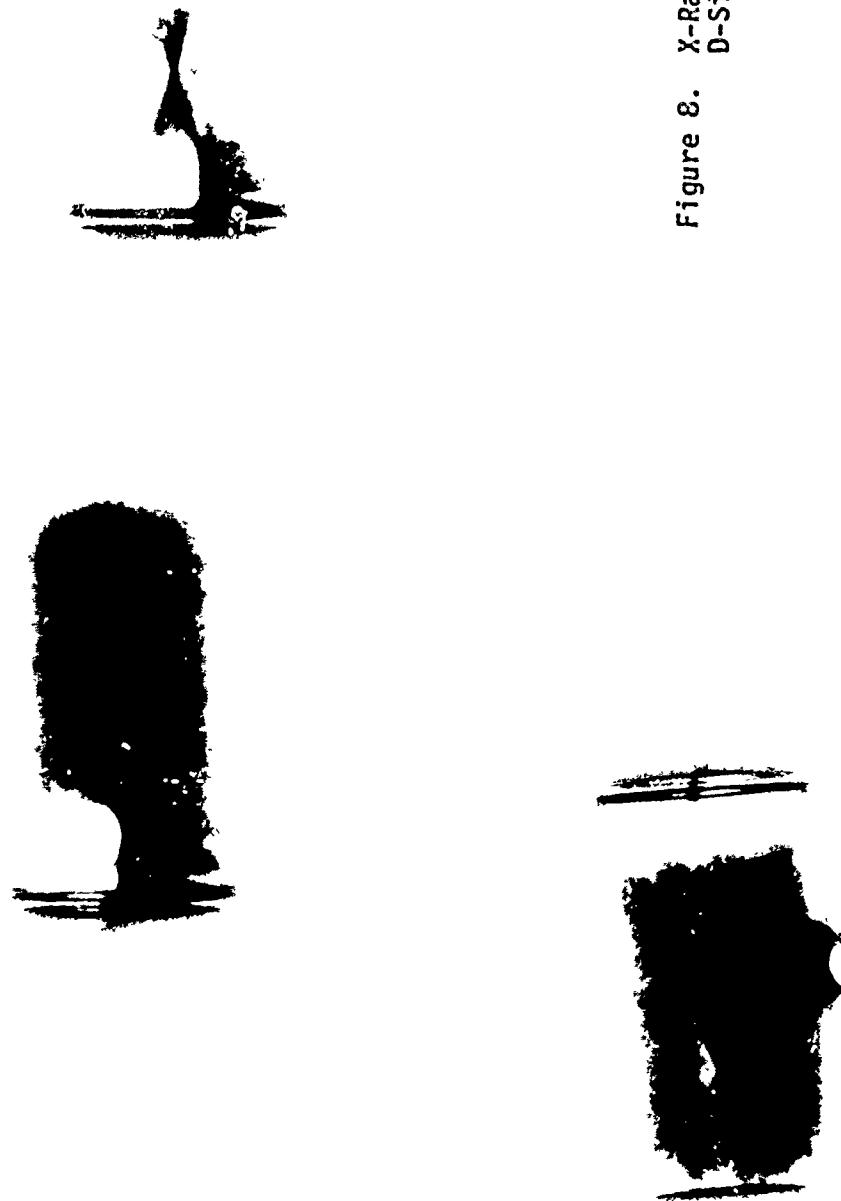
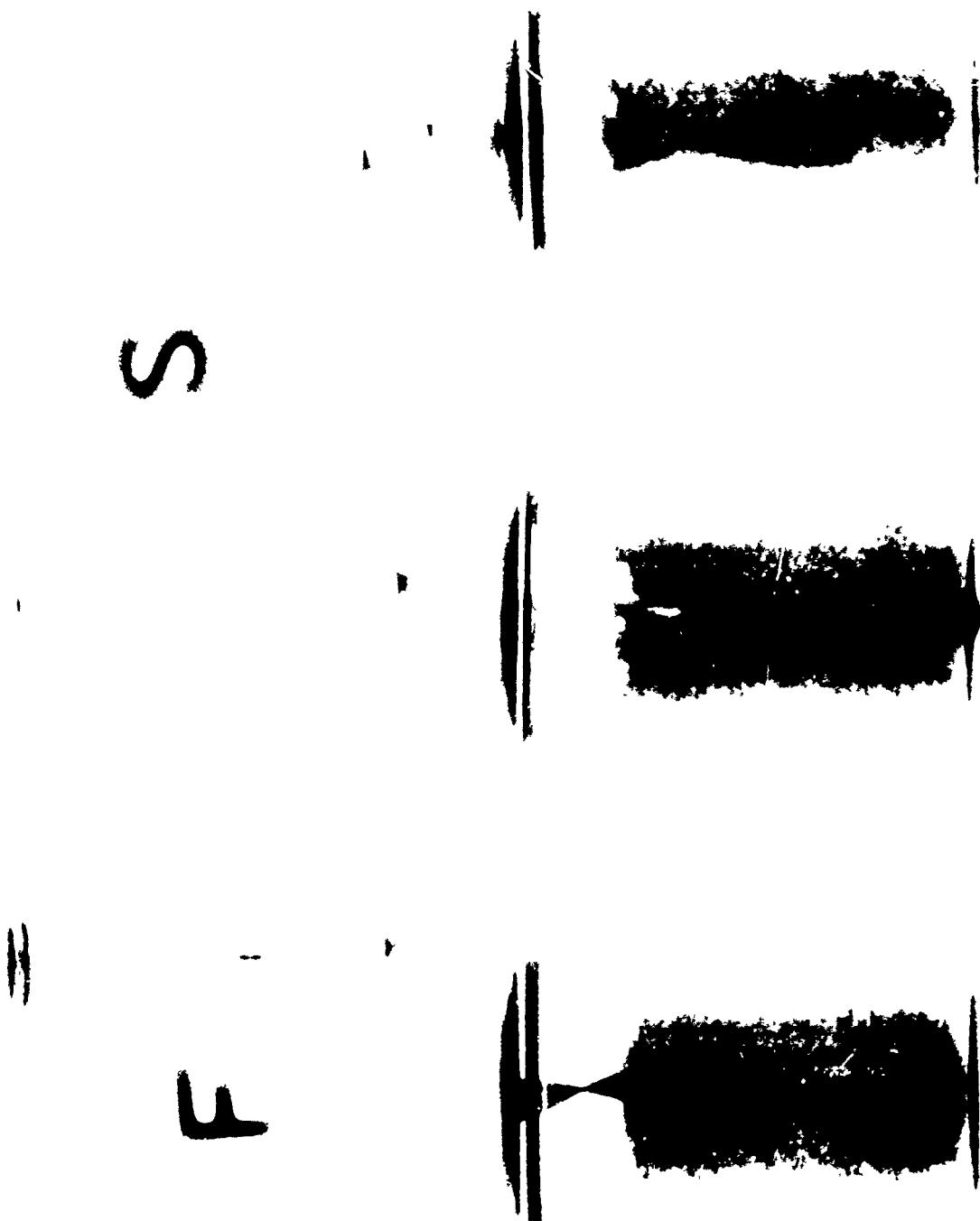


Figure 9. X-Ray of Both AA and D-Sized Cells



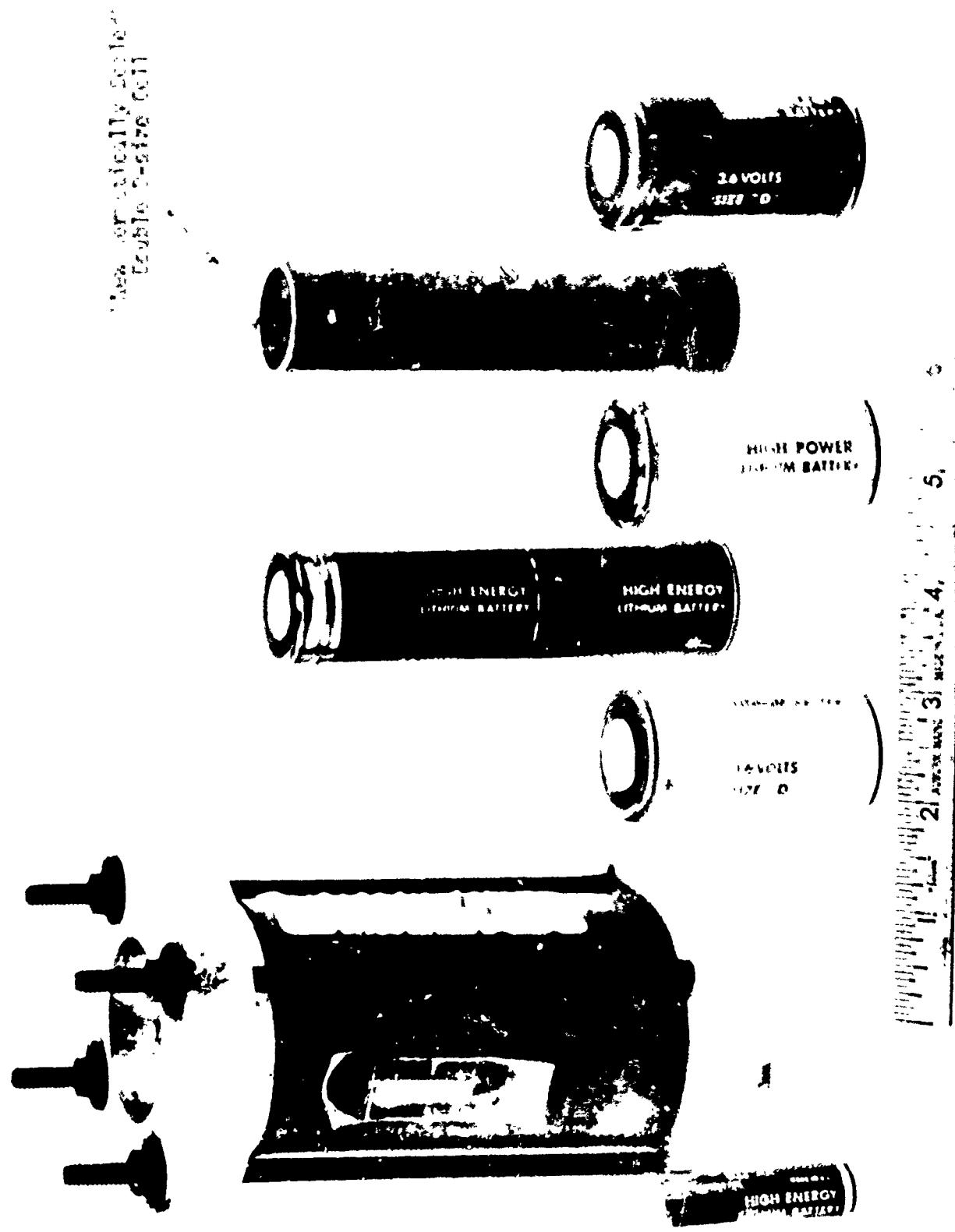


Figure 10. Four Types of Lithium Batteries Tested

TABLE III
Summary of Cell Performance

| TEST | CELL | TEST CONDITIONS | DISCHARGE RATE | DISCHARGE TIME | AMPERE HOURS | MAX VOLTS | FINAL VOLTS |
|------|------------------------------------|--------------------------------------|----------------|--------------------|--------------|-------------|-------------|
| 1.a | High Energy AA (sealed) | 3 runs at different discharge rates | 1m amp | 58.5 min | .001 | 3.619 | 3.54 |
| 1.b | High Energy AA (sealed) | battery at 5°C | 10m amp | 60 min | .01 | 3.515 | 3.44 |
| 1.c | High Energy AA (sealed) | (abnormally high rates) | 100m amp | 2 hrs | .2 | 3.0 | 2.98 |
| 2 | High Energy AA (sealed) | low rate, long term run at 5°C | 1.65mamp | 42 days | 1.68 | 3.4 | 2.8 |
| 3 | High Energy D size | life test at 5°C | 80m amp | 110 hrs | 13.44 | 2.95 | 1.38 |
| 4.a | High Energy D size cell #22 | low rate, long term run at 2°C | 4.5mamp | 11 days | | 3.545 | 3.51 |
| 4.b | High Energy D size cell #23 | low rate, long term run at 2°C | 4.5mamp | 127 days | | 3.549 | 3.51 |
| 4.c | High Energy D size cell #24 | low rate, long term run at 2°C | 4.5mamp | 124 days | | 3.523 | 3.51 |
| 5 | High Energy D size, two cells | trickle charging 3 Gates cells | .4mamp | 2 yrs | | 7.2 | |
| 6 | High Energy D size | determine effect of orientation | 40m amp | 163 hrs | 8.913 | 3.486 | 3.22 |
| 7 | High Energy D size | 5 short periods of high temp storage | 40m amp | over a 8 dy period | 8.268 | 3.652 | 3.44 |
| 8 | High Energy D size | life test after high temp storage | 5m amp | 100 days | Approx 12 | 3.615 | 1.3 |
| 9 | High Power D size | life test at 5°C | 80m amp | 136 hrs | 11.2 | 3.3 | 3.0 |
| 10 | High Power D size (S_2Cl_2) | life test at 5°C | 80m amp | 99.5 hrs | 7.1 | 3.53 | 3.0 |
| 11.a | High Power D size | life test (in silicon oil) | 2.76 amp max | 1.85 hrs | 4.6 | 3.037 | 1.4 |
| 11.b | High Power D size (S_2Cl_2) | life test (in silicon oil) | 2.98 amp max | 1.30 hrs | 3.5 | 3.255 | 1.7 |
| 12 | High Power D size | room temp life test | .3 amp | 31.5 hrs | 9.4 | 3.34 | 2.88 |
| 13 | High Power D size (S_2Cl_2) | room temp life test | variable | 27 hrs | 8.7 | 3.37 | 3.0 |
| 14 | High Power D size | pulse mode | variable | 11 hrs | | | |
| 15 | High Power D size (10 cells) | simulate laser designator power pac. | pulse 5 amp | 50 pulses | | 28 at pulse | |
| 16 | High Energy Double D size | room temp life test | 160mamp | 166 hrs | 26.6 | 3.476 | 3.0 |
| 17 | High Energy Double D size (sealed) | room temp life test | 160mamp | 234 hrs | 32.4 | 3.412 | 0.70 |
| 18 | High Energy Double D size (sealed) | life test at 5°C | 160mamp | 124.5 hrs | 19.75 | 3.401 | 3.0 |
| 19 | Experimental high energy low rate | life test at 2°C | 45mamp | 1843 hrs | 82.94 | 3.51 | 2.88 |
| 20 | High Energy D size (2 cells) | discharge after long term storage | 40mamp | 101 hrs | 4 | 1.7 | |

TABLE III
Summary of Cell Performance

| | DISCHARGE RATE | DISCHARGE TIME | AMPERE HOURS | MAX VOLTS | FINAL VOLTS | REMARKS |
|------|----------------|--------------------|--------------|-----------|-------------|---|
| tes | 1m amp | 58.5 min | .001 | 3.619 | 3.549 | Voltage rose during test. |
| | 10m amp | 60 min | .01 | 3.539 | 3.442 | Voltage dropped during test. |
| | 100m amp | 2 hrs | .2 | 3.0 | 2.917 | Voltage nearly constant during test. |
| | 1.65mamp | 42 days | 1.68 | 3.4 | 2.8 | Voltage remained above 3 volts for 40.5 days. |
| | 80m amp | 168 hrs | 13.44 | 2.95 | 1.31 | |
| | 4.5mamp | 121 days | | 3.545 | 3.338 | |
| | 4.5mamp | 127 days | | 3.549 | 3.334 | Noticed effect of battery sleeping. |
| | 4.5mamp | 124 days | | 3.523 | 3.001 | |
| | .4mamp | 2 yrs | | 7.2 | | Charged Gates cells initially & still trickle charging them. |
| | 40m amp | 163 hrs | 8.913 | 3.486 | 3.225 | Battery performance sensitive to orientation. |
| rage | 40m amp | over a 8 dy period | 8.268 | 3.652 | 3.497 | Strong voltage resonance after high temp storage. Some capacity lost. |
| | 5m amp | 100 days | Approx 12 | 3.615 | 1.3 | Seven day storage at 71°C. Voltage stable during discharge. |
| | 80m amp | 136 hrs | 11.2 | 3.3 | 3.0 | . |
| | 80m amp | 99.5 hrs | 7.1 | 3.53 | 3.0 | Poor quality of S ₂ Cl ₂ . |
| | 2.76 amp max | 1.85 hrs | 4.6 | 3.037 | 1.4 | Maximum temperature of cell 43°C. |
| | 2.98 amp max | 1.30 hrs | 3.5 | 3.255 | 1.7 | Poor quality of S ₂ Cl ₂ . Maximum temperature of cell 40°C |
| | 3 amp | 31.5 hrs | 9.4 | 3.34 | 2.987 | Voltage steady during test. |
| | variable | 27 hrs | 8.7 | 3.37 | 3.001 | 1 hr at .9 amps, 2 hr. at .5 amps, . hrs at .2 amps, 20 hrs at .3 amp. |
| | pulse variable | 11 hrs | — | | | Pulsed at various rates between 5 and 8 amps. |
| | pulse 5 amp | 50 pulses | 28 at pulse | | | 1 min on, 1 min off. Tested at 49°C. |
| pack | 160mamp | 166 hrs | 26.6 | 3.476 | 3.0 | |
| | 160mamp | 234 hrs | 32.4 | 3.412 | 6.705 | 156.5 hours (25.2 ampere-hours) above 3.0 volts. |
| | 160mamp | 124.5 hrs | 19.75 | 3.401 | 3.0 | 78% lower capacity when discharged at 5°C. |
| | 45mamp | 1843 hrs | 82.94 | 3.51 | 2.885 | Turned upside down and ran for 2131 hours (96.2 amp-hrs). |
| | 40mamp | 101 hrs | 4 | 1.7 | | Indicates damaging effect of passivation film. |

2

Test 2

An AA sized cell was discharged completely to determine the total ampere-hours available. The test ran for 42 days and resulted in a capacity of 1.68 ampere-hours for a discharge rate of 1.65 milliamperes. Figure 11 shows the discharge characteristics of this cell.

Test 3

A long duration life test was run on a high energy D size cell at 5°C. The test lasted for 168 hours at a constant 80 milliampere discharge rate resulting in a 13.44 ampere hour capacity.

Test 4

Three high energy D size batteries were subjected to a low rate long term discharge test at a temperature of 2°C. The batteries were placed in a very quiet environment in the refrigerator. About 30 days into the test cell number 23 seemed to be fading and over a ten day period the voltage continually dropped. However, a very slight tap on the battery case with a pencil point revived the battery. This effect is termed "sleeping." The voltage stayed fairly constant for the duration of the test. All three batteries delivered 4.5 milliamperes of current at a voltage above 3 volts for over 120 days. Figure 12 shows the discharge curve for battery number 23 and the sleeping phenomenon is clearly seen.

Test 5

Two high energy D-size cells are currently trickle charging three Gates, sealed, rechargeable lead-acid batteries (x size). The two lithium inorganic

SIZE AA LITHIUM CELL

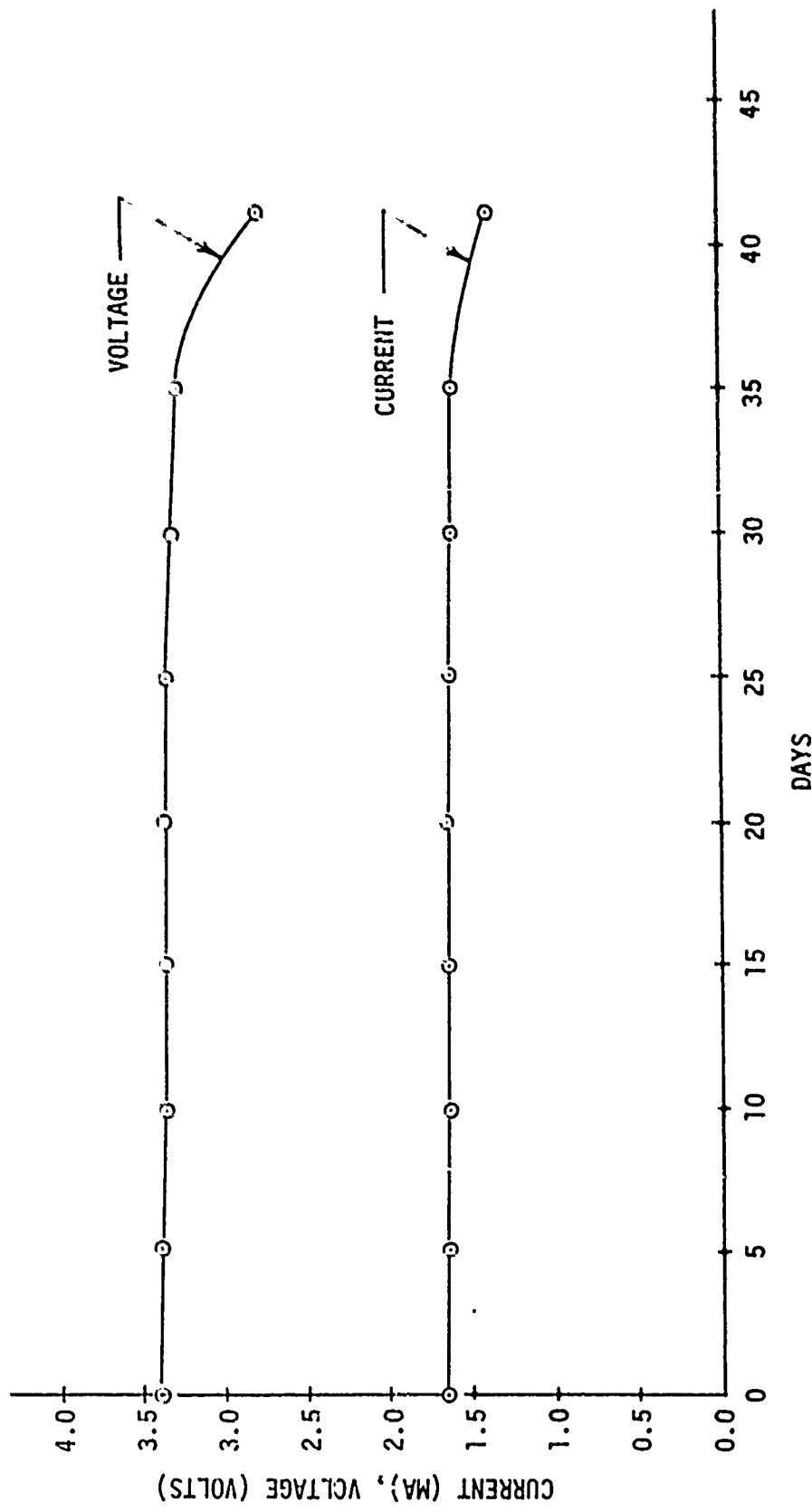


Figure 11. Discharge Characteristics of AA Sized Cell

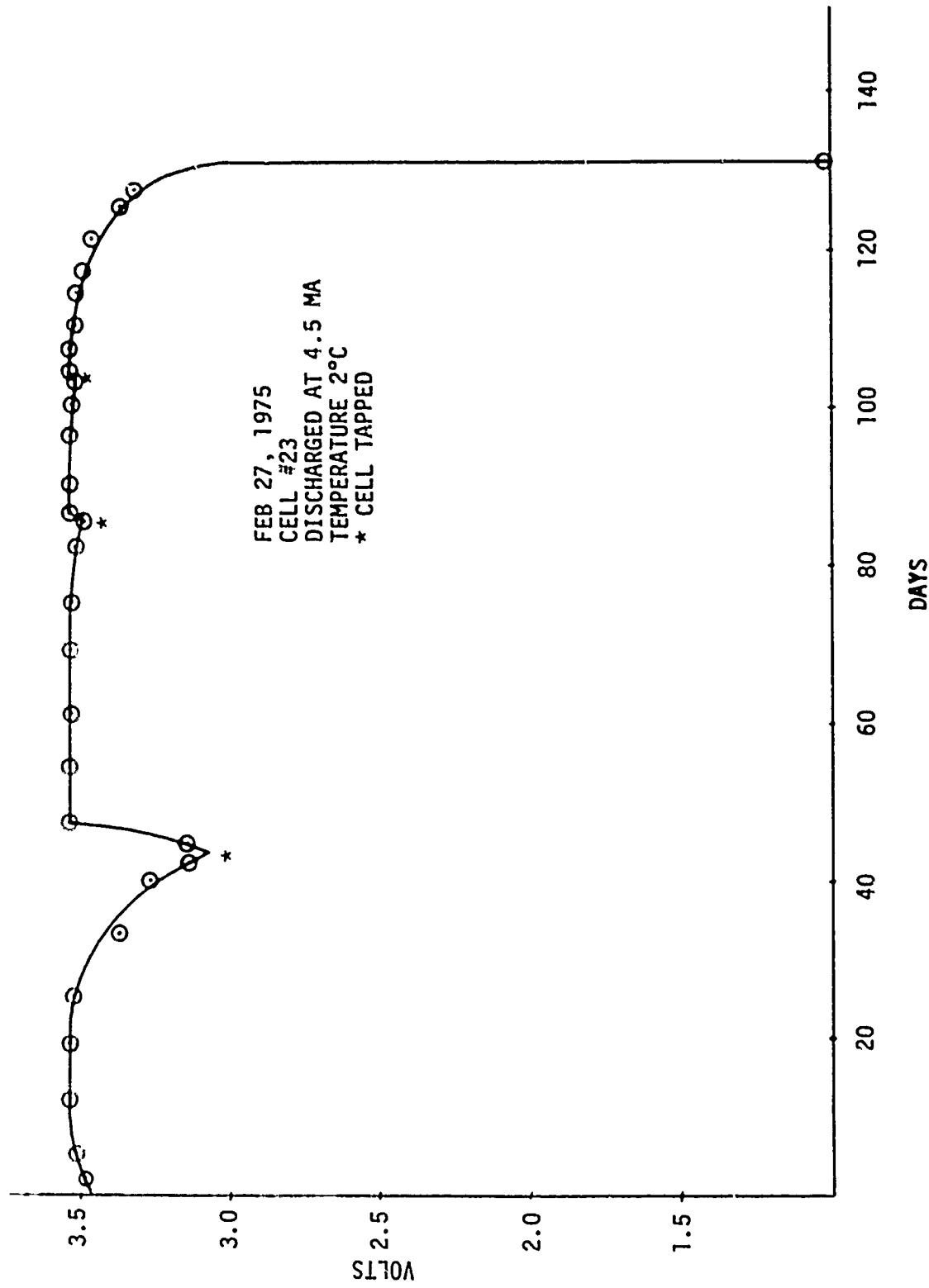


Figure 12. Discharge Characteristics of D Sized Cell Showing Sleeping

cells, at the present discharge rate, should keep the three Gates cells fully charged for a period of up to two years. The lithium batteries had to first recharge the Gates cells since they had been in storage for about a year. To initially recharge the Gates cells required up to 4 milliamperes at 7.2 volts for a period of 13.5 days at room temperature. All 5 cells were then placed in the refrigerator at 5°C and eventually the current was reduced to 0.4 milliamperes for the long term trickle charging test (eight months have elapsed so far). The objective of this test is to show the feasibility of combining the good low rate performance of the lithium cells with the good high rate performance of the lead acid cells. The self-discharging characteristics of the lead acid batteries can be prevented with this scheme. For deep ocean applications (0°C), the recharging voltage required by the three lead acid cells is exactly that delivered by two lithium batteries which greatly simplifies the recharging circuit (see Figure 13). The Gates cells are nominally 2 volts with a capacity of 5 ampere-hours. Possible applications for this arrangement are deep ocean transponders and sound sources.

Test 6

One important discovery was the sensitivity of the cell to orientation. The 10 ampere-hour cell exhibited full capacity in the vertical position with the positive terminal upward. However, it lost 33 percent of the capacity in the horizontal position and 66 percent in the vertical position with the positive terminal down, a result of the physical arrangement of electrodes and electrolyte in the cell. As liquid electrolyte is converted to solid product in the cathode, a significant electrode area is no longer wetted and capacity

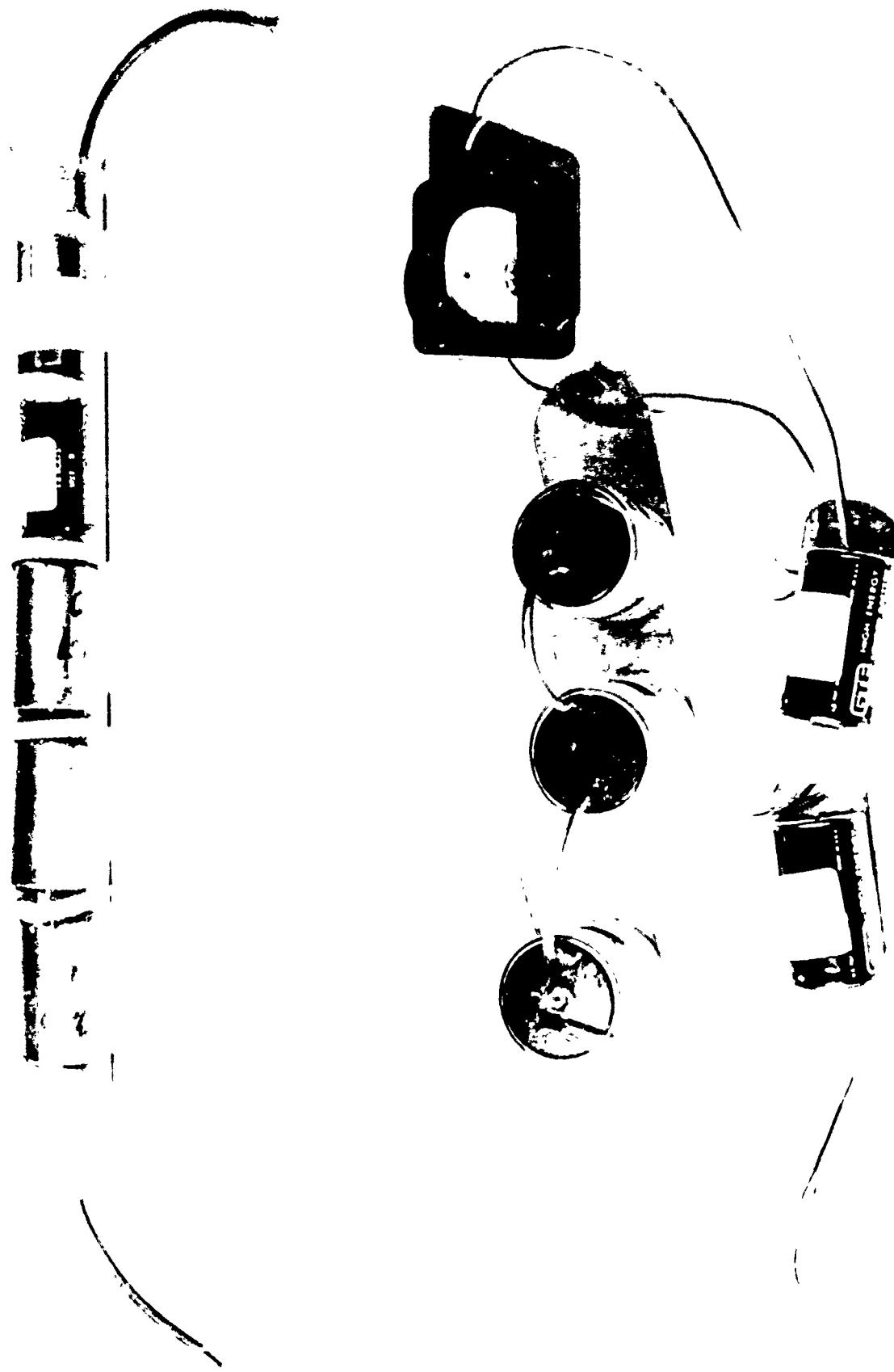


Figure 13. Two Lithium Batteries Recharging Three Gates Lead Acid Cells

is lost. Another example of this effect is shown in Figure 14. While the cell was kept horizontal the capacity was about 6.05 ampere-hours. However, when placed vertically another 1.77 ampere-hours resulted. A total of 8.9 ampere-hours was obtained from this cell.

Test 7

A high energy D-size cell was heated in a desiccator at five different temperatures and the discharge characteristics were observed after each temperature increment. The total time spent at any temperature was about six hours and the five temperatures were 42°C, 48.5°C, 60°C, 71°C, and 75°C. After being stored for six hours at one of the temperatures the battery was allowed to cool to room temperature, then connected to a load (40 milliamperes) and the voltage was monitored for a half hour. The discharge characteristics during this period were very stable and showed that the battery can support a constant 40 millampere current load at over 3.5 volts after short periods of high temperature storage. The total ampere-hours obtained from this battery was 8.268 which includes this high temperature test and some post-test discharges at 40, 100 and 180 milliamperes (all above 3 volts). There was some deterioration of the battery capacity during the test (<30%).

Test 8

Three high energy D-size cells were placed in storage for seven days at 71°C then completely discharged at 5 milliamperes. The first cell lasted 96 days, the second lasted 103 days and the third lasted 105 days. The voltage was very stable (above 3.5) during this period. This period of high temperature storage did not appear to damage the cells nor affect their performance.

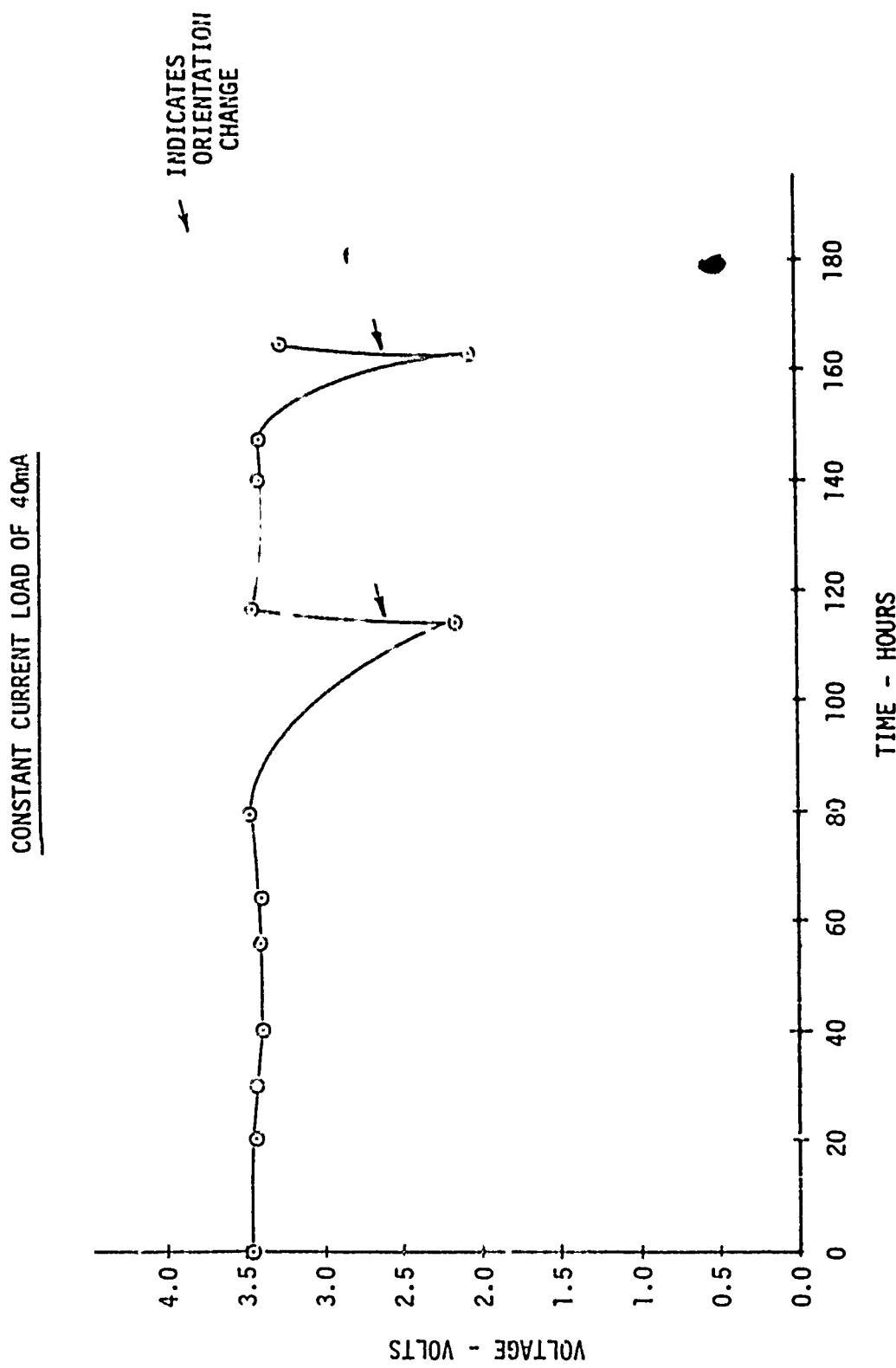


Figure 14. Lithium Battery Orientation Sensitivity

Test 9

A life test was conducted on a high power D-size cell at 5°C. The test lasted for 136 hours and produced 11.2 ampere-hours above 3.0 volts. The discharge current was 80 milliamperes and the voltage was very stable above 3.0 volts as shown in Figure 15.

Test 10

Sulfur monochloride, S_2Cl_2 , (explained in detail under the Hazard Tests Section) has been added to some of the high power cells in an effort to prevent the battery from exploding at high temperatures by dissolving the solid sulfur generated during normal discharge. With S_2Cl_2 present, the life of the battery is reduced, down to 99.5 hours with a capacity of only 7.1 ampere-hours. This reduced performance (63% reduction compared to Test 9) has been traced to be the result of using low purity S_2Cl_2 (not vacuum distilled). In Test 13 vacuum distilled S_2Cl_2 was used and the performance was significantly improved.

Test 11

Two high power D-size cells were discharged through a one ohm resistor to compare their discharge characteristics for an undersea vehicle application. One cell contained sulfur monochloride and the other did not. The current nearly reached 3 amperes for both cells during the test. As expected the cell without the sulfur monochloride outperformed the other cell (1.85 hours and 4.6 ampere-hours versus 1.3 hours and 3.5 ampere-hours). This large difference in performance is again attributed to the use of non-vacuum distilled S_2Cl_2 .

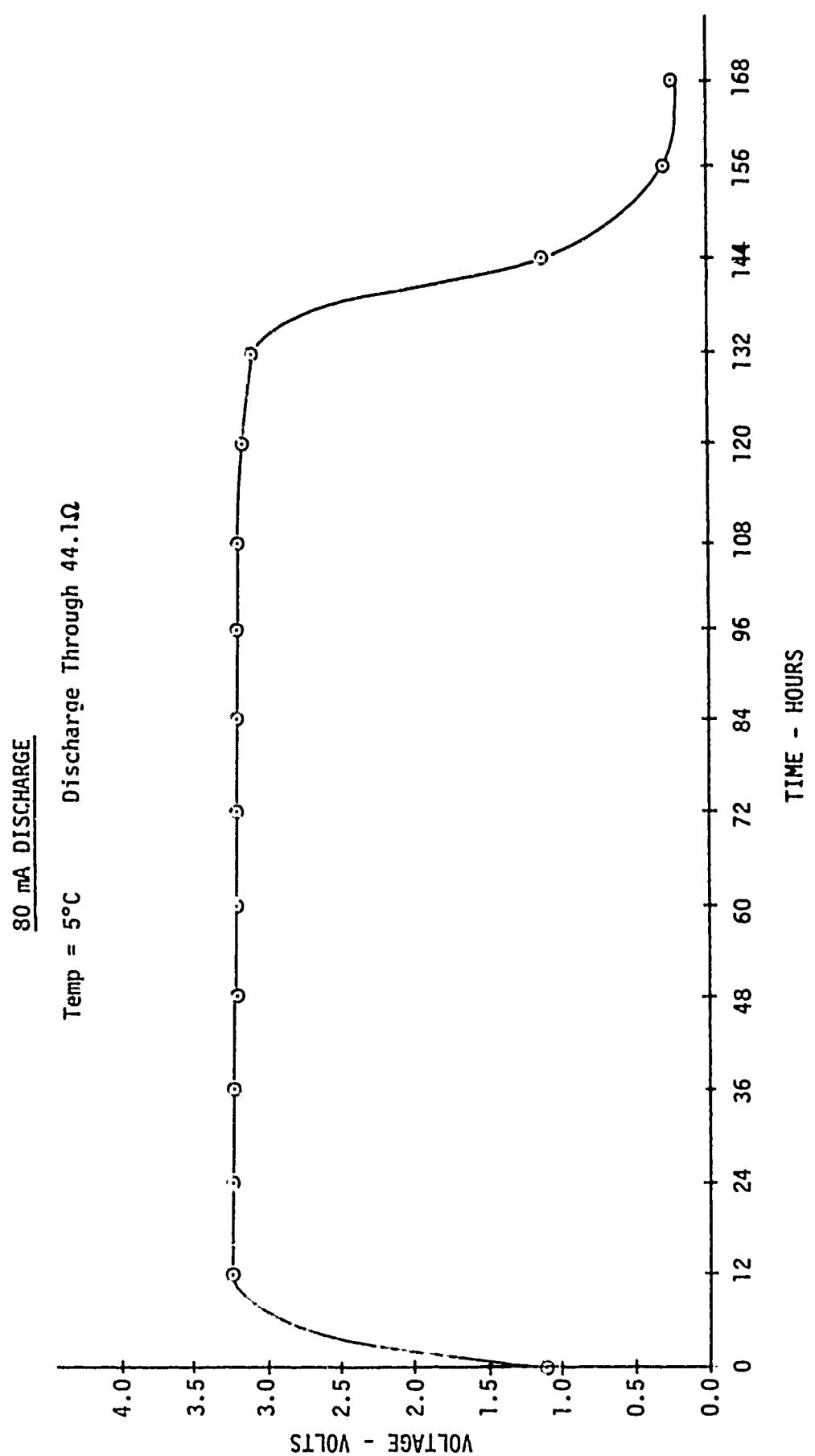


Figure 15. High Power Cell Discharge Characteristics

Test 12

For this life test a high power D size cell without S_2Cl_2 was discharged at 0.3 amperes. The ampere-hours above 3 volts was 9.4 during a 31.5 hour discharge.

Test 13

This high power D size cell contained high purity vacuum distilled S_2Cl_2 . The cell was discharged at various rates (1 hour at 0.9 amperes, 2 hours at 0.5 amperes, 4 hours at 0.2 amperes and 21 hours at 0.3 amperes). The test lasted for 27 hours and showed that cells containing purified sulfur monochloride can provide 92% of the capacity of cells without sulfur monochloride. The ampere-hours were 8.7 and the watt-hours per pound were calculated at 137.

Test 14

An attempt was made to get 30 ampere pulses from a high power D size cell for an active sonobuoy. The results of a pulse test showed that the cell could deliver 7.9 ampere pulses at 2.4 volts. The pulse was on for 6 seconds and off for 30 seconds. A one ampere quiescent load was also applied to simulate the receiver power requirement. The test lasted for eleven hours and the pulse current varied from 5 to 8 amperes. Even though only 7.9 ampere pulses were obtained it should be possible to get 30 ampere pulses by increasing the electrode surface area four times. It is feasible to increase the existing anode surface area (30 in^2) to 120 in^2 such that it will fit in the standard D-size casing. This should increase the discharge rate by four times but correspondingly decrease the cell life.

Test 15

Ten high power D-size cells were connected in series and used to simulate the power pack of a Modular Universal Laser Equipment (MULE). The requirements for this test were to have the cells pulse for as long as they maintained a voltage of greater than 20 volts while delivering five ampere pulses. The pulses were on for one minute and off for one minute. The test was conducted in the desert sun at the Naval Weapons Center, China Lake, California where the battery temperature was 63°C before the test. The lithium battery pack delivered 50 satisfactory pulses. During the pulse on time the voltage dropped to 28 volts but instantly rose to 36 volts when the pulse was turned off. The current during the pulse was between 6 and 6.5 amps. The battery temperature had increased to 78°C at the final pulse. The currently used NiCd battery pack delivered 10 pulses when tested under the same conditions.

Test 16

A life test was conducted on a double D size cell at room temperature. The cell discharged through a 160 milliamperc load for 166 hours resulting in a capacity of 26.6 ampere-hours.

Test 17

This high energy double D-size cell had the new hermetic seal. The life test lasted for 156.5 hours above 3.0 volts which resulted in a battery capacity of 25.2 ampere-hours above 3.0 volts. The test was continued for as long as possible to see just how much ampere-hour capacity the battery contained. After 234 hours (with the voltage under one volt) the test was stopped and the ampere-hours obtained was 32.4. Figure 16 shows the results of this test.

DOUBLE D HIGH ENERGY LITHIUM CELL WITH HERMETIC SEAL

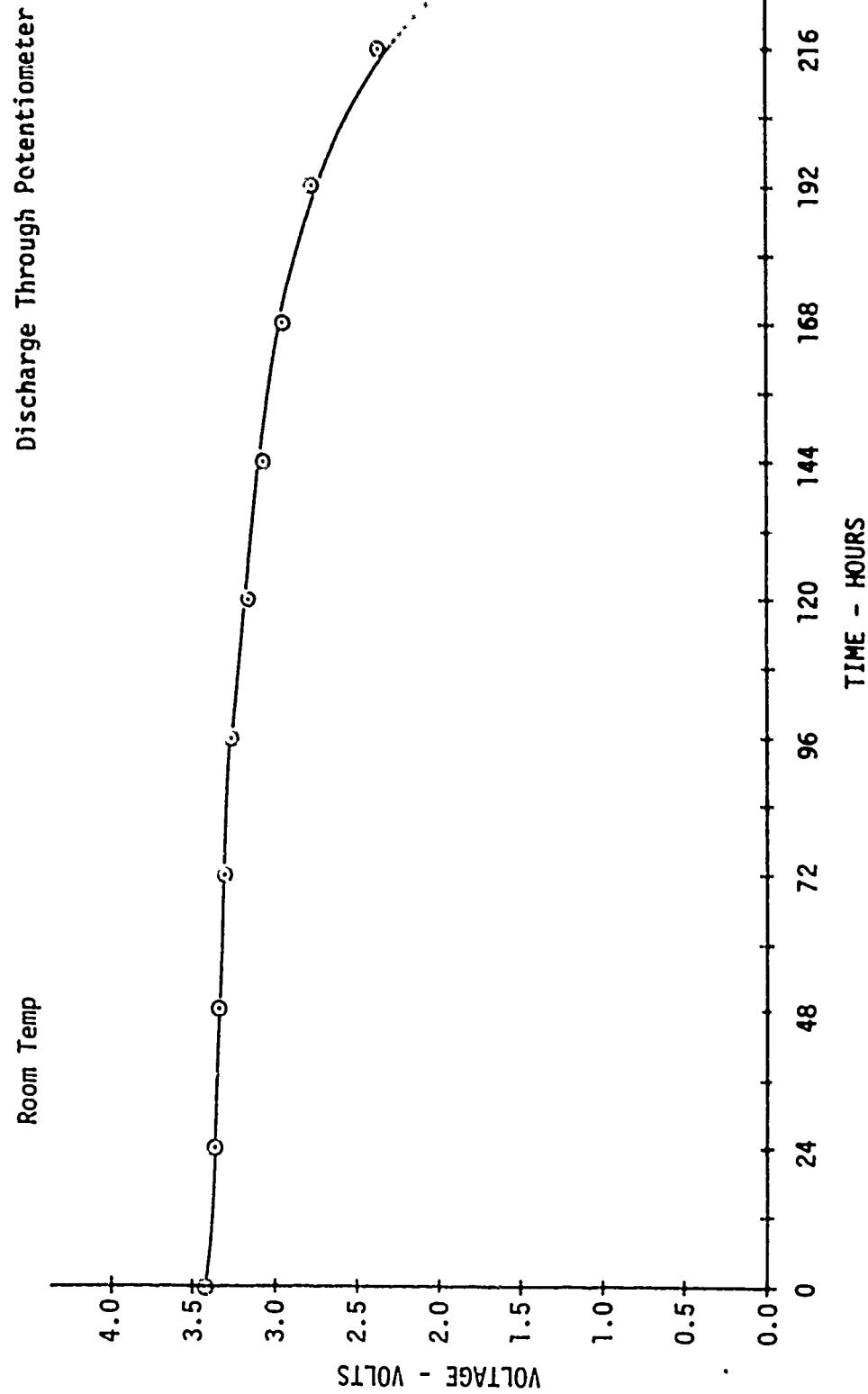


Figure 16. Life Test of Hermetically Sealed Double D-Sized Cell

Test 18

A life test was conducted on a high energy sealed double D-size cell at 5°C to compare with the data taken at room temperature from Test 17. This test lasted for 124.5 hours above 3.0 volts giving a capacity of 19.75 ampere-hours above 3.0 volts. At the end of the test (after 192 hours) the voltage dropped below one volts and the total capacity was 28.7 ampere-hours. The useful ampere-hours with the battery at 5°C was 78% of that at room temperature. Figure 17 shows the performance of the cell.

Test 19

The largest cell tested was an experimental 100 AH, low rate cell. This cell was discharged at a rate of 45 milliamperes for a total of 1843 hours (82.94 ampere-hours). At this point the voltage noticeably decreased so the cell was turned upside down and continued to discharge for another 288 hours giving a total capacity of 96.2 ampere hours. The curve showing the first 1843 hours of discharge is shown in Figure 18. This test data shows the ability to scale up cell design using available mathematical models. This cell design is described in Appendix A.

Test 20

Two high energy D size cells with old style crimped seals were discharged after being stored for over eight months at room temperature. The first test just determined how long it would take an extensively passivated cell to come up to 3 volts at a 40 milliampere discharge rate, and the second test was a life test on a passivated cell. Both tests were conducted at 5°C. It took the first cell 1.7 hours to reach 3 volts and another 5.5 hours to reach a maximum of 3.43 volts at a discharge rate of 10 milliamperes.

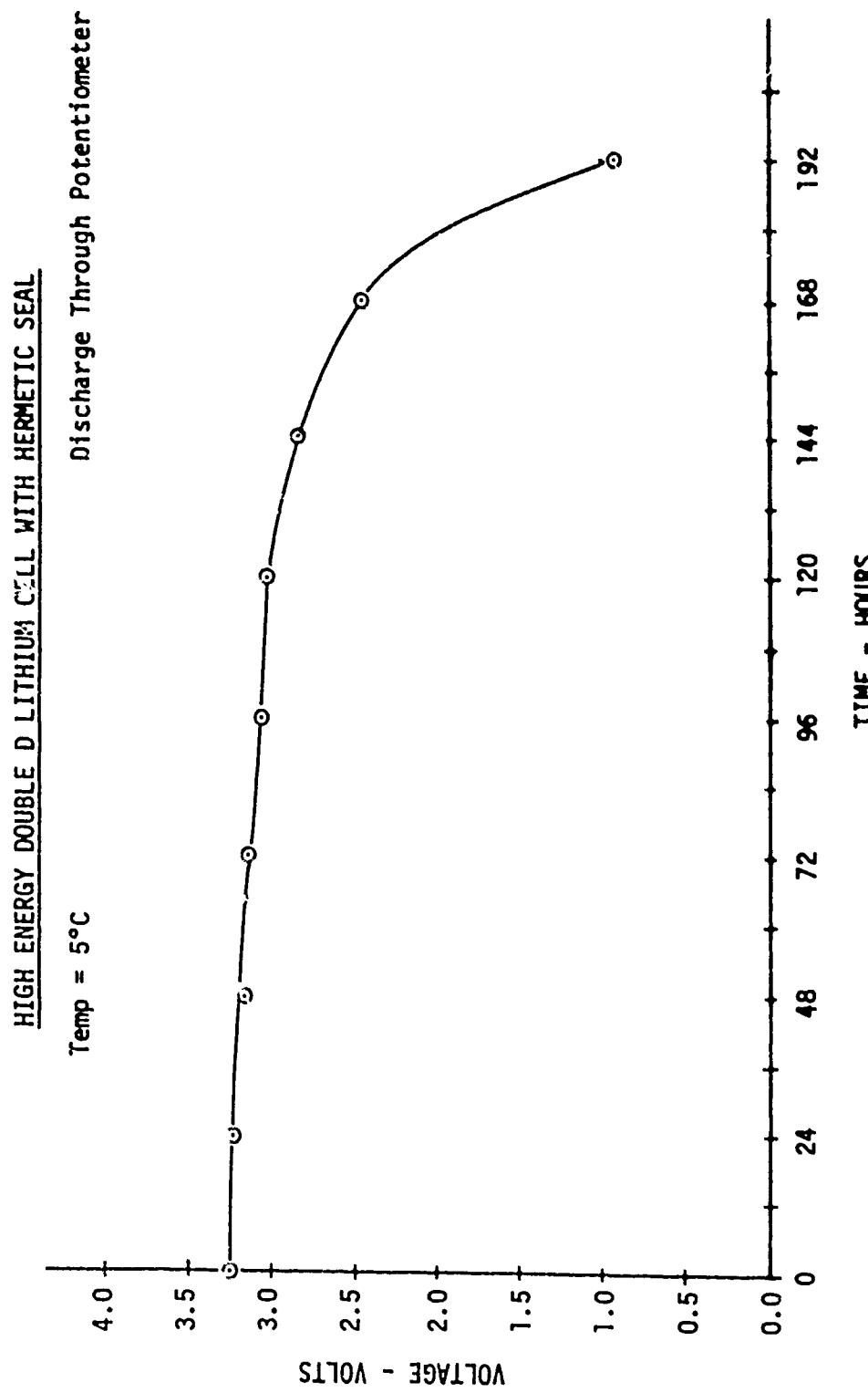


Figure 17. Life Test of Hermetically Sealed Double D Size Cell at 5°C

HIGH ENERGY LITHIUM INORGANIC CELL (100 AMP-HR.)

Constant Discharge Rate of 45 mA

Temp = 5°C

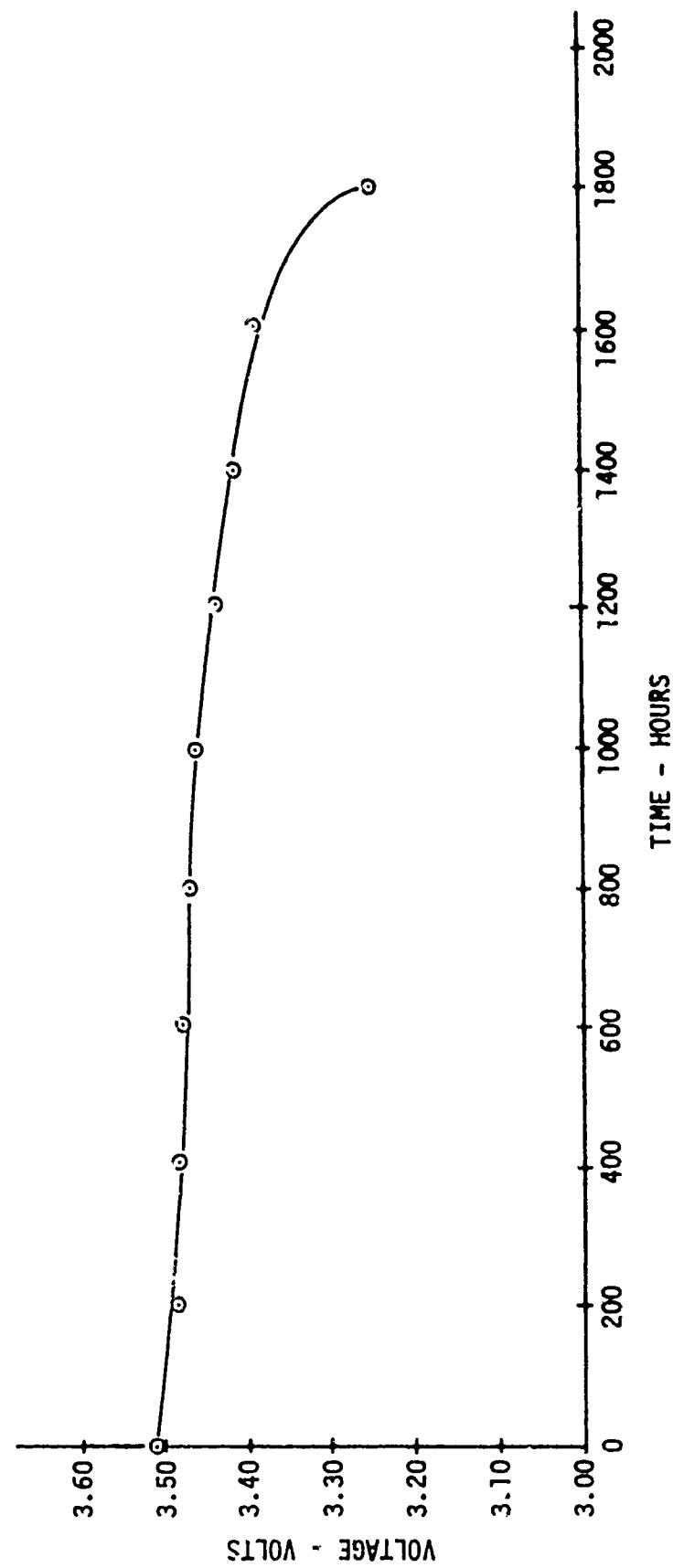


Figure 18. Discharge Characteristics of Experimental 100 AH Cell

The second cell was stored for nine months and never did reach 3 volts. This cell was discharged at a rate of 40 milliamperes and only reached a maximum voltage of 1.7 volts. The cell discharged for 101 hours resulting in a cell capacity of 4 ampere-hours.

The results of our test effort indicates that the major contributing factor to cell passivation is the moisture from the atmosphere entering the cell through the crimped seal. When this happens hydrochloric acid (HCl) is formed from the reaction between water and thionyl chloride. This acid attacks the lithium forming lithium-chloride (LiCl) one of the ingredients of the passivating film. With two of the major cell components (lithium and thionyl chloride) slowly being reacted it is expected that the cell will be degraded.

Atmospheric moisture may be only one of several mechanisms of passivation, as the complete mechanism of passivation is not yet understood. However, certain aspects of it can be described. The lithium reacts with the electrolyte or its products forming small crystals of lithium chloride that are mechanically bonded to the lithium. The presence of this film of lithium chloride crystals prevents the flow of electrons between the anode and electrolyte. However, its presence does not completely block the flow of lithium ions as evidenced by at least some small voltage when the cell is connected to a circuit.

During normal battery use this film will slowly be removed. As the lithium metal becomes oxidized the lithium ion migrates to the thionyl chloride and it is the ions closest to the thionyl chloride that undergo this reaction. But, these are the same ions that are holding the passivating film in place.

Hence, there will be a tendency for the crystals to be undermined and fall off as the battery is being discharged. It is possible that a dead short placed on the cell for about a minute may be enough to remove most of the crystals in the passivating film.

Since the film is only mechanically bonded to the lithium it can be mechanically removed. The three ways presently used to accomplish this are:

(a) applying heat or cold to the cell to cause a thermal expansion of the lithium, (b) applying pressure (200 psi) to an uncompensated cell, and (c) applying a mild vibration to the cell. A better understanding of the nature of the film will be needed before an effective way can be found to remove or control the growth of the passivation film. Lithium chloride may not be the only constituent of the passivation film.

In our tests of cells with the new hermetic seal no passivation has been noticed. Small AA sized cells that have been stored for 3 months start at voltages over 3 volts when discharged through a load. The new Double D size cells have not exhibited any passivation problems, but they were only recently acquired.

Environmental Test Series

When the lithium battery receives wide acceptance by the Navy it may involve applications that impose extreme storage, transport or operational environments. A series of environmental tests were conducted to determine the effect on these batteries from various environmental hazards. These include external pressure (applied to both an uncompensated and compensated battery), vibration, shock, and humidity.

Pressure

The first test conducted was a pressure test on a modified, pressure-compensated cell. To pressure compensate the cell a small hole was drilled in the top (through the positive terminal). A fluorocarbon fluid, Dow FC-75, surrounded the hole to prevent moisture in the air from entering the cell and reacting with the electrolyte and lithium. The cell with its bath of FC-75 was placed upside down in a glass jar and suspended from the lid of the oil filled pressure tank. Wires were connected to the electrodes, soldered to connectors in the tank cover and fastened to a voltmeter and ammeter.

The cell performance was shown to improve after the application of pressure as indicated by the volt-ampere curves taken both before and after the pressure was applied. Table IV shows this performance increase.

By applying pressure to an uncompensated cell it is possible to alter the depassivation process. A modest pressure of 200 psi is enough to show the effect of some depassivation. Further improvement results when the pressure is increased to 450 psi. At these pressures the cell case is deformed enough to cause some of the passivating film to lose its bond with the lithium anode

TABLE IV
Improved Cell Performance Under Pressure

| TEST | APPLIED PRESSURE | VOLTAGE DECREASED FROM | AS CURRENT WAS INCREASED FROM |
|------|------------------|------------------------|-------------------------------|
| A | 0 psi | 3.58 to 2.6 | 4 to 100 ma |
| | 1000 psi | 3.5 to 3.15 | 4 to 100 ma |
| | 2000 psi | 3.55 to 3.1 | 4 to 100 ma |
| B | 0 psi | 2.6 to 0.1 | 4 to 360 ma |
| | 2000 psi | 3.6 to 0.1 | 4 to 940 ma |
| | 5000 psi | 3.55 to 0.2 | 4 to 800 ma |

and the discharge rate can be increased. No cell case damage resulted at these low pressures. When much larger pressures (3000 to 5000 psi) were applied there was no noticeable effect on depassivation. However, both ends of the cell were severely deformed. The top cap (positive terminal) was pushed down about 3/16 inches (except for the epoxy ring) and the entire bottom was caved in. The discolored oil bath and odor of sulfur dioxide indicated a leak in the battery.

Table V summarizes the results from this test. The increase in discharge rate indicates that the depassivation process was enhanced as a result of the applied pressure.

Vibration

The next series of tests were vibration tests. Five D-size cells were placed in a test fixture with different orientations and subjected to vibrations of various frequencies. Table VI shows the test schedule and results of the vibration test. The horizontally oriented cell showed the most stable, as well as, highest voltage during the vibration test. The higher frequency test had the most detrimental effect on the cells. Two of them showed a marked drop in voltage. The test was stopped because of the presence of gas, probably from cell #4. It should be noted that the voltage actually increased for the cells when they were subject to a low frequency vibration similar to that found on board ship.

TABLE V
Cell Depassivation Under Pressure

| CURRENT, MA | VOLTAGE | | | | |
|-------------|---------|---------|---------|----------|----------|
| | 0 PSI | 200 PSI | 450 PSI | 3000 PSI | 5000 PSI |
| 4 | 2.6 | 3.46 | 3.55 | 3.46 | 3.42 |
| 10 | 0.3 | 3.32 | 3.45 | 3.41 | 3.4 |
| 20 | | 3.12 | 3.3 | 3.25 | 3.21 |
| 30 | | 2.55 | 3.2 | 3.12 | 3.08 |
| 40 | | 2.48 | 3.1 | 3.0 | 2.93 |
| 50 | | 1.1 | 2.95 | 2.85 | 2.8 |
| 60 | | 0.4 | 2.85 | 2.7 | 2.6 |
| 70 | | | 2.7* | 2.51 | 2.4 |
| 80 | | | 2.45 | 2.35 | 2.0 |
| 90 | | | 1.9 | | |
| 100 | | | | | |

TABLE VI
Cell Vibration Test Results

| Vibration | | | Voltage | | | | |
|--------------|--|-----------|---------|---------|---------|---------|---------|
| Freq. | Amplitude | Duration | Cell #1 | Cell #2 | Cell #3 | Cell #4 | Cell #5 |
| 0 | 0 | 0 | 3.46 | 3.15 | 3.51 | 2.96 | 3.33 |
| 5 hz | 0.03" | 5 min | 3.46 | 3.15 | 3.51 | 2.95 | 3.33 |
| 10 hz | 0.03" | 5 min | 3.46 | 3.16 | 3.51 | 2.95 | 3.33 |
| 15 hz | 0.03" | 5 min | 3.46 | 3.20 | 3.51 | 2.95 | 3.33 |
| 20 hz | 0.02" | 5 min | 3.46 | 3.21 | 3.51 | 2.95 | 3.33 |
| 25 hz | 0.02" | 5 min | 3.46 | 3.22 | 3.51 | 2.96 | 3.33 |
| 30 hz | 0.01" | 5 min | 3.46 | 3.21 | 3.51 | 2.97 | 3.33 |
| 35 hz | 0.005" | 5 min | 3.46 | 3.20 | 3.51 | 2.98 | 3.33 |
| 40 hz | 0.005" | 5 min | 3.47 | 3.20 | 3.5 | 2.98 | 3.33 |
| 45 hz | 0.003" | 5 min | 3.47 | 3.20 | 3.52 | 2.99 | 3.33 |
| 50 hz | 0.003" | 5 min | 3.47 | 3.20 | 3.52 | 2.99 | 3.33 |
| Freq. range | | Amplitude | | | | | |
| 5 to 17 hz | 0.1" peak to peak | | 3.47 | 2.77 | 3.51 | 2.30 | 3.19 |
| 17 to 28 hz | 1.5g decrease | | 3.47 | 2.8 | 3.51 | 2.31 | 3.22 |
| 28 to 44 hz | 0.036" peak to peak | | 3.47 | 2.73 | 3.51 | 0.86 | 3.22 |
| 44 to 500 hz | 3.5g decrease | | 3.47 | 2.72 | 3.51 | 0.94 | 3.22 |
| 500 to 44 hz | 3.5g increase from zero to 0.036" peak to peak | | 3.47 | 2.72 | 3.51 | 0.97 | 3.22 |

Cell orientation: #1-Vertically up, #3-Horizontal,
#2-Vertically down, #4-45° up, #5-45° down

Shock

Cell #4 was removed from the test fixture for the shock tests. The remaining four cells were connected in series with a potentiometer to vary the current load. Both voltage and current were displayed. Table VII gives the shock loadings and voltages both before and after the shock impact. Only very slight voltage decreases were noticed after each shock test and on one test a small negative voltage spike appeared at the instant of shock impact. The volt-ampere curve taken just after the series of shock tests was only slightly lower than that taken before the test.

Humidity

Nine high energy D-size cells were placed in a vacuum desiccator with one Normal of NaOH to absorb the gasses that leaked through the battery seal. This procedure was an attempt to quantify the HCl and SO₂ gasses escaping from the cell seal. The result of this test indicated that the cell seal was extremely porous to both the gaseous products of hydrolysis and atmospheric moisture. The amount of gas present in the desiccator was so large that no quantitative measurement could be made. This is because moisture from the environment entered the cell through the seal, and reacted with the cell components severely corroding the tops of several cells. The test lasted four days and was conducted at three different temperatures (2°C, 20°C, and 55°C). In each case the humidity in the desiccator was 100%. Figure 19 shows the cells after being removed from the desiccator. Long term exposure to atmospheric moisture results in complete cell corrosion as shown in Figure 20. The new cells containing the hermetic seal are not expected to exhibit this behavior.

TABLE VII
Cell Shock Test Results

| Test | Acceleration | Current Load | Shock Loading | | | Voltage | Remarks |
|------|--------------|--------------|---------------|-------|--|---------------------|---------|
| | | | Before | After | | | |
| 0 | 0 | | 13.69 | | | | |
| 1 | 15 to 25g | 30 ma | 13.69 | 13.69 | | No voltage drop | |
| 2 | 125 to 175g | 30 ma | 13.69 | 13.65 | | | |
| 3 | 15 to 25g | 60 ma | 13.07 | 13.02 | | | |
| 4 | 125 to 175g | 60 ma | 13.92 | 13.01 | | Small voltage spike | |
| 5 | 15 to 25g | 100 ma | 12.22 | 12.18 | | | |
| 6 | 125 to 175g | 100 ma | 12.18 | 12.15 | | | |
| 7 | 125 to 175g | 100 ma | 12.15 | 12.13 | | | |

Figure 19. Effect of 100% Humidity for Four Days

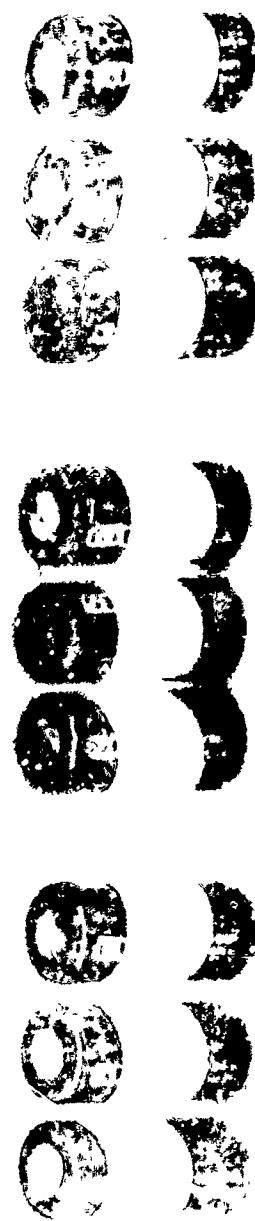


Figure 20. Complete Cell Corrosion Following 9 Months Storage



Cell Disposal in Seawater

To estimate the environmental impact of cell disposal in seawater, a discharged cell was placed in a bucket of seawater. The residual cell current formed a galvanic cell which caused severe pitting and corrosion on the cathode current contact. Two and one half hours later the cathode terminal corroded completely through and the voltage rapidly dropped from 3.5 volts to 0.42 volts. By observing this demonstration it is possible to hypothesize the results from cell disposal in the ocean. The residual electrolytic action will first rupture the seal (on the non-hermetically sealed cells). Seawater will then enter the battery and react with its components. The lithium will react with the seawater to form LiOH and H₂. The thionyl chloride will react with the seawater to form SO₂ and HCl. These gasses and acids will leave the battery and enter the water column and dissolve or pass through it (depending upon the depth of disposal). The nickel from the case will be solubilized by the acids and electrolytic action and precipitate out as (NiOH)₂. After a period of time all that remains will be teflon from the seal, rust from the iron in the can, the graphite plug and the plastic wrapper. The lithium will return to its natural state, LiCl, by the reaction LiOH + HCl → LiCl + H₂O. Sulfites, one of the nutrients in the food chain, will be formed by the action SO₂ + H₂O + H₂SO₃.

Hazard Tests

Three potential hazards facing users of high power cells are excessive heat, punctured cells and short circuits. Tests indicate that high power cells will explode when exposed to any of these hazards. Two other possible hazards, although not yet tested, are the effect of a dead cell in a parallel or series circuit and the effect of a charging current on a cell.

Heat

The purpose of this test was to determine at what temperature an unloaded high power cell will explode. The cell was placed in a bath of silicone oil and heated. After 23 minutes, at a temperature of 168°C, the cell exploded.

Puncture

Six high power cells and one double D-size cell were ruptured by a nail to determine the effect on these cells from a puncture. The test apparatus allowed a weight to be remotely released and fall on a nail driving it into the cell. Of the seven tests conducted, four resulted in an explosion. Table VIII summarizes the results of this test.

From these tests it is possible to hypothesize a mechanism which accounts for these violent explosions. As the nail penetrates the battery the relatively malleable lithium is easily deformed into thin filaments or fibers along the shaft of the nail. As these lithium filaments are forced deeper into the battery by the action of the nail they make contact with the graphite cathode producing a direct internal short. All the electrical current produced by the

TABLE VIII
Cell Puncture Test

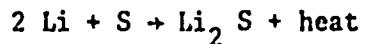
| | |
|---|---------------------|
| High power - fresh | Immediate explosion |
| High power with S_2Cl_2 - fresh | Immediate explosion |
| High power - partially discharged | Immediate explosion |
| High power with S_2Cl_2 - fully discharged | No explosion |
| Double D | No explosion |
| High power, shorted - partially discharged | No explosion |
| High power with S_2Cl_2 - slightly discharged | Immediate explosion |

cell will be discharged at these sites which will rapidly heat the lithium filaments to their melting point. This same intense current will also form elemental sulfur from the decomposition of the thionyl chloride. When the molten lithium fibers come in contact with the elemental sulfur a thermite-like reaction is initiated. This reaction may produce a temperature as high as 1600°C. Several high temperature reactions may now occur. Among these are the unraveling of the teflon, the oxidation of the cathode, and the decomposition of the thionyl chloride; all of which tend to feed the reaction. The result is a rapid pressure excursion produced by the reaction products which ultimately ruptures the cell case and the explosion scatters the reactants.

Short Circuit

Experience with cells of the high power configuration (high rate) indicates that when shorted these cells will generate sufficient current to heat the lithium to its melting point (179°C). When this happens the cell will detonate. Table IX summarizes these tests.

Laboratory experiments confirmed the fact that the reaction between molten lithium and sulfur is exothermic. The equation is



The thermite-like reaction gave off a white light indicating a temperature of approximately 1500 to 1600 degrees Celcius. At this high temperature, reactions not normally considered became important. Such as the thermal decomposition of teflon to produce highly reactive gases. When one considers that

TABLE IX
Summary of Cell Short Circuit Tests

| BATTERY | TEMP MAX | TIME MIN. | CURRENT AMPS | REMARKS |
|--|-------------|--------------|-----------------|----------------------------------|
| 1. High Power P1 | 124°C | 10 | | explosion |
| 2. High Power P2 | 154°C | 9 | 20 | destroyed metal box |
| 3. High Power P5 | 128°C | 12 | 21 | no damage to cast iron container |
| 4. High Power P4 | 90°C | | | in oil bath, no explosion |
| 5. High Power (S_2Cl_2) | 113°C | | | case bottom bulged out |
| 6. High Energy Double D size (insulated) | 110°C | | | end cap ruptured |
| 7. Series of ten High Power Cells | | | | detonation of all cells |
| 8. High Power P8 | 153°C | 11 | | explosion |
| 9. High Power PM1 | 142°C | 5 | 22.5 | end cap blew off with a fire |

the cell at the time of discharge contains two-thirds of the ingredients of gun powder and the chemical production of an oxidizing agent is possible by a large number of reactions, the fact that an explosion occurs is not surprising. It is clear that the thermite-like reaction between lithium and sulfur is the match that initiates the explosion.

Test 1

A high power cell was short circuited to see how long it would take to detonate and at what temperature the cell case increased to during the discharge. The cell detonated ten minutes after the circuit was closed at a case temperature of 124°C.

Test 2

For this test a D size high power cell was placed in a box in an effort to contain the explosion. The 18 pound box was made from 1/16 inch mild steel (one side was 1/8 inch aluminum) with a 1/4 inch clear Lexan cover. During the short circuit discharge the terminal voltage of the cell dropped to about one volt, the current reached 20 amperes and the temperature increased to a maximum of 154°C. After nine minutes the cell exploded severely damaging the container as shown in Figure 21. The box was thrown to a height of 33 feet carrying instrumentation wires and a strip chart recorder.

Test 3

A cast iron container (5 inches diameter, 9 inches long and 3/8 inch thick) designed to transport explosive bolts was used in this test as a means to contain the explosion. A high power cell was placed in the container and short

Figure 21. Battery Container Damage by Short Circuit Test



circuited. The current peaked out at 21 amperes and the temperature increased to 129°C. Twelve minutes into the test the cell exploded. The container suffered no damage.

Test 4

A high power cell was short circuited in a small bath of silicone oil. The cell temperature only increased to 90°C after 5 minutes then began to decrease. The cell did not detonate; possibly, because a convective cell was set up in the oil to keep the battery cool.

Test 5

A modified high power cell containing sulfur monochloride was short circuited without any explosion. The only damage was that the bottom cell end cap was bulged out. The maximum temperature was 113°C.

Test 6

A high energy double D-size cell with a crimp seal was insulated in paper towels and short circuited. After a temperature rise to 110°C the cell end cap ruptured and forced out the battery components.

Test 7

Ten high power cells were connected in series and placed inside a vented pressure cooker to contain the explosion. Five to seven minutes after the circuit was shorted the first battery detonated and smoke appeared at the vent. Three more batteries detonated at about one minute intervals producing a solid stream of flame at the vent. Seconds later the remaining batteries exploded blowing the lid off the pressure cooker and scattering the battery remains.

Test 8

Test 8 and 9 were conducted under similar conditions to compare the effect of a cell containing sulfur monochloride and one without the additive. The high power cell without sulfur monochloride detonated 11 minutes after the circuit was shorted. Figure 22 shows the debris from this test. The maximum temperature was 154°C and the current reached a peak of 16 amperes. Figure 23 shows a graph of both the current and temperature during the test.

Test 9

The high power cell modified with sulfur monochloride did not detonate when shorted, rather its end cap ruptured and a fire resulted. Figure 24 shows the remains of this cell. This test only lasted 5 minutes until the case ruptured with a temperature rise to 116°C and a max current of 22.5 amperes. Following cell rupture, the temperature recorder indicated 142°C. Figure 25 shows the temperature and current data from this test.

As a result of laboratory tests, it was found that if the sulfur was in solution the melted lithium did not react with it. From this observation, it was clear that if a good solvent for sulfur was added to the battery that could keep the sulfur in solution and not alter the electrical characteristics, then the detonation could be prevented. A solvent that met these criteria was sulfur monochloride (S_2Cl_2). When one sixth of the thionyl chloride was replaced by S_2Cl_2 the cell did not explode when shorted. A comparison of cell remains from short circuit tests are shown in Figures 22 and 24. Notice the case of the cell containing S_2Cl_2 is still in one piece.

Figure 22. Debris from Short Circuit Test on High Power Cell



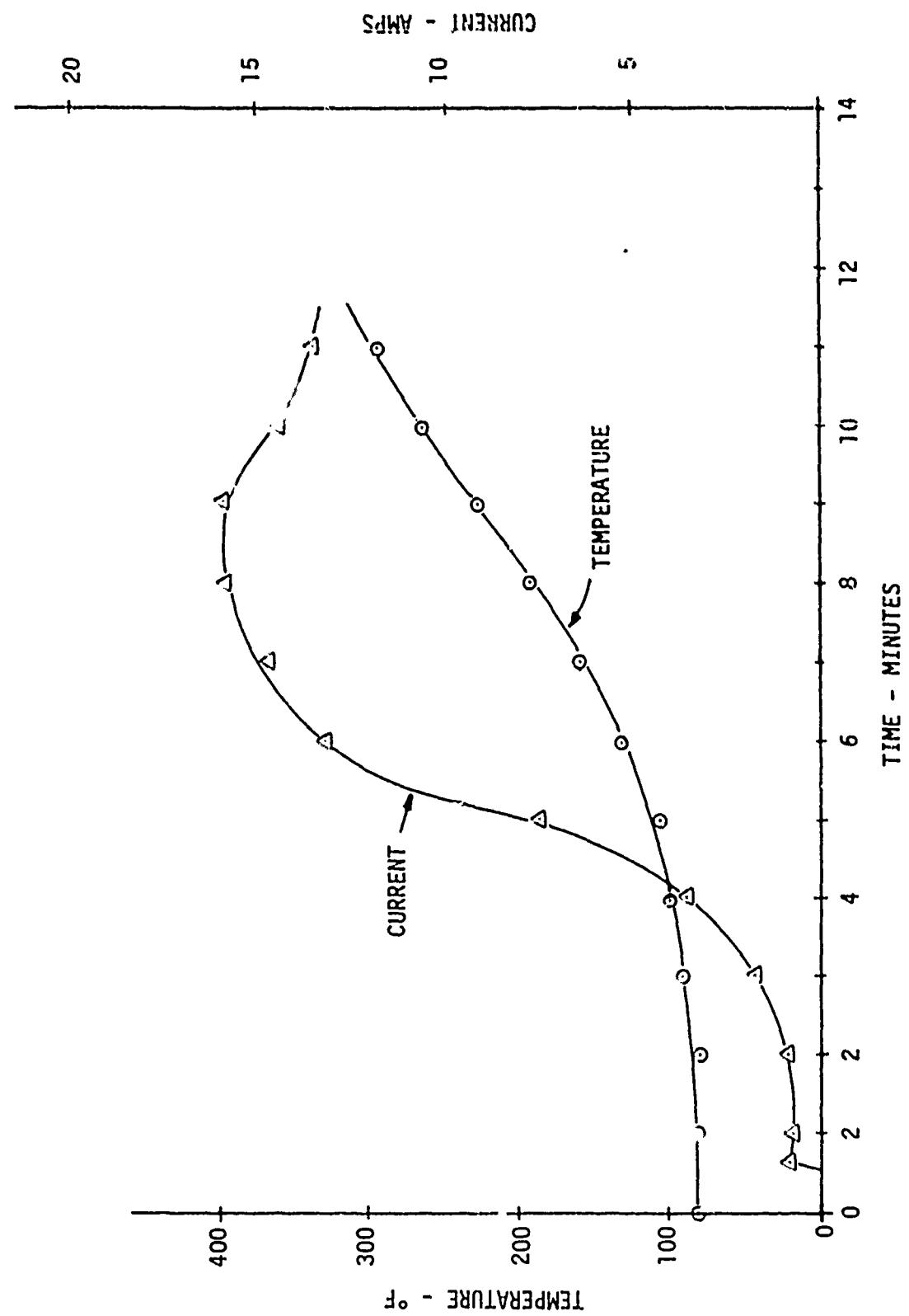


Figure 23. Temperature and Current Data During High Power Cell Test

Figure 24. Debris from Short Circuit Test on Modified High Power Cell



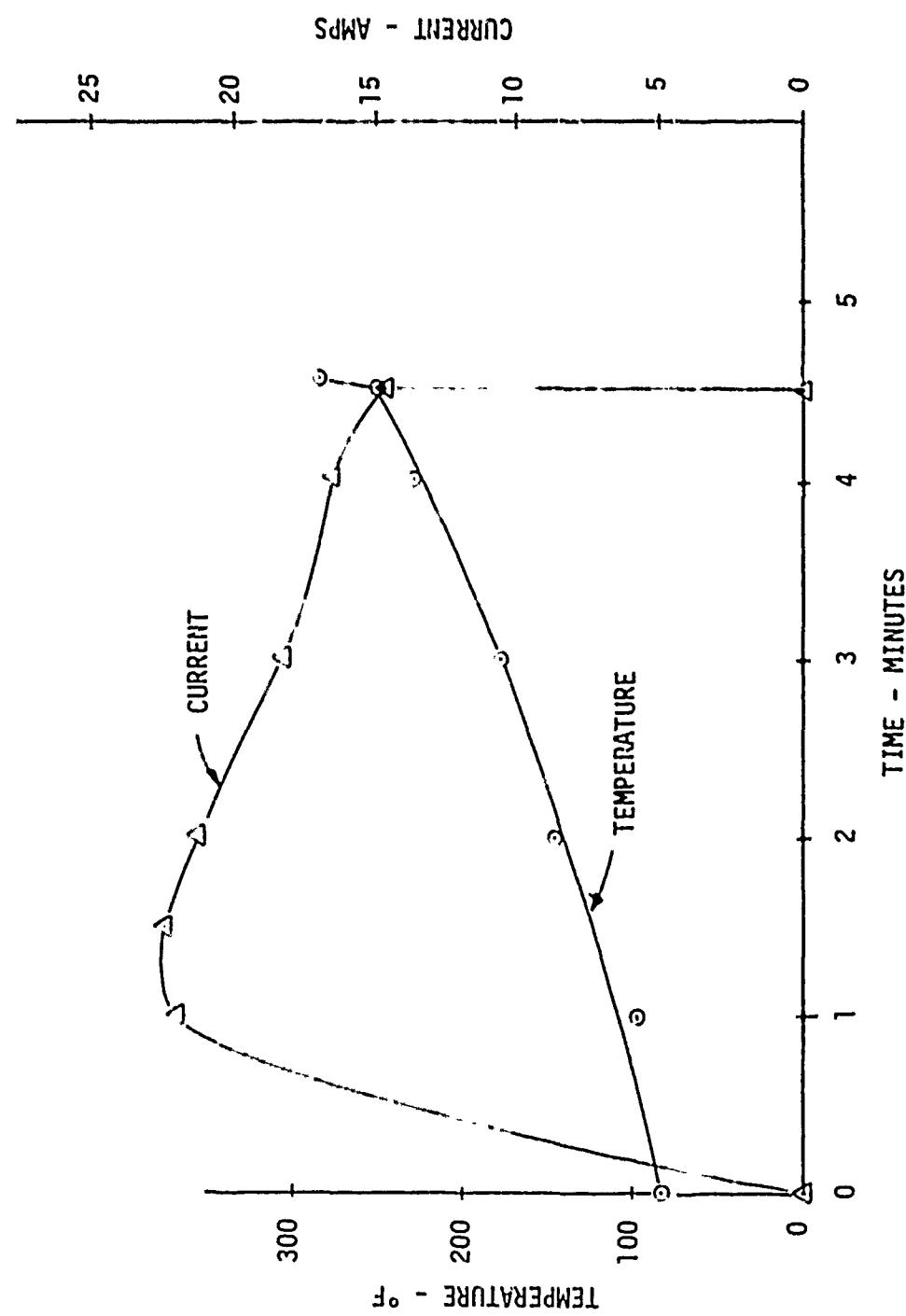


Figure 25. Temperature and Current Data During Modified High Power Cell Test

From these data it is clear that there are two ways to prevent an explosion. One is to keep the temperature of the battery below the melting point of lithium, and the second is to introduce a solvent for sulfur such as sulfur monochloride. Field tests of both of these methods demonstrated that the detonation of the cells could be prevented by either method (Tests 4 and 5).

Summary of Test Results

The bulk of the testing effort utilized the D-size cell with a crimped seal. Fresh D-size high energy cells provided the manufacturers specified performance only at low current discharge rates of 100 milliamperes or less. Cell voltage prematurely decreases to below cutoff values when discharge rates are greater than 100 milliamperes on "D" size cells. This means that "D" size High Energy cells should not be applied in applications having a continuous discharge life less than 5 days. Ideal applications should have discharge periods of weeks or months for maximum cell efficiency.

The performance tests were conducted at both room temperature and at 5°C with discharge rates varying from 5 to 100 milliamperes. Good performance and long life were achieved above 3 volts for a majority of the cells tested.

Short storage periods (less than three months) at room temperature (less than 25°C) do not adversely affect the performance of cells with crimped seals. However, longer periods (over eight months) have a very damaging effect on the cell by causing corrosion around the seal and reducing cell ampere-hour capacity. In addition, these cells severely passivate when stored for a long time resulting in a significant voltage delay. The extreme case involves the nonhermetically

sealed cells stored outside (in a metal chest) for one year. In this case corrosion was complete and cell capacity reduced to zero. The hermetically sealed cells are not expected to have this problem.

Another problem is that these cells seem to be sensitive to cell orientation during discharge. Maximum capacity is possible with the cell vertically upright with minimum capacity resulting when the cell was vertically oriented with the positive terminal down. Any method that will allow the electrolyte to wet the electrodes will prolong the cell discharge life.

Another phenomenon, related to orientation sensitivity, is cell sleeping when discharging in a very quiet environment. This was observed in some tests and results in a premature decrease in cell voltage due to the clogging of the cathode or interelectrode region by products of the reaction which reduces electrolyte contact with the electrodes.

The high power configuration (high rate) is more prone to explode than the high energy configuration. These high power cells will explode within 15 minutes if short circuited (discharging at a rate of about 20 amperes without cooling). They will also explode when exposed to a temperature slightly above 160°C (for about 1/2 hour) and when punctured rapidly by a sharp object. The explosion liberates a large quantity of white gas, probably vaporized thionyl chloride. This gas quickly hydrolyzes because of the moisture in the atmosphere and forms acids of HCl and SO₂. Two methods that have been demonstrated to prevent the explosion are to keep the cell cool during high rate discharge and to use an additive such as sulfur monochloride to dissolve the elemental sulfur produced during normal discharge.

High humidity has such a disasterous effect on steel cased cells (complete case corrosion within a year) that submerging the cells in seawater has been shown as a rapid means of disposing of the cells.

Shock and vibration did not degrade the performance of the high energy cells, at least not at the frequencies normally found on board ship.

Likewise, the effect of pressure on a pressure compensated cell does not harm the cell (actually the performance improves because the electrolyte can more thoroughly wet the electrode surface area). Pressure equalization results in higher current densities from the cell electrodes.

Other methods that could be used to achieve higher current cells for propulsion and pulse power applications are to increase the electrode surface area by using large area thin electrodes or possibly hermetically sealing the cell to prevent the escape of high pressure gaseous discharge products from the cell.

Voltage delay, experienced with cell that have been stored for long periods of time, can be overcome by shocking the cell either physically or thermally (high temperature or very low temperature). Hydrostatic pressure (~200 ft depth) also de-passivates cells.

The new hermetically sealed cells are expected to be free of the problem of case corrosion and diminished cell capacity due to long term storage, particularly in a humid environment. The new cells are also anticipated to show a higher volt-ampere performance, no sleeping and be less subject to passivation after storage.

Cells of 100 ampere-hours have been built and successfully tested. Cells with capacities up to 10,000 ampere-hours could be similarly designed that would be relatively economical for many military applications that require large amounts of energy.

APPLICATION EXPERIENCE

Numerous possible applications of the lithium-Inorganic cells have been investigated. These applications include Moored Surveillance Buoys, Directional Command Active Sonobuoys, Expendable Sound Source Buoys, Deep Ocean Acoustic Navigation Transponders, NavFac Lightweight Array Cable Test Program, Marine Corps Man-Portable Battlefield Radar Sets, Laser Designators, Mobile Sound Simulators, Geophysical Monitoring Balloons, Submarine Target Location Balloon Transmitters, Marine Mammal Implantable Biotelemetry packages, Arctic Sensor Buoys, torpedoes, and Advanced Untethered Deep Ocean Search Systems. Each of these applications could benefit from the use of Lithium-Inorganic batteries but decisions to use these batteries have been dependent on the test results from this program.

As a result of test experience with these cells and the resulting design improvements that have been accomplished to date, multicell batteries are being introduced to the fleet for certain applications.

At the present time cell capabilities and limitations must be carefully compared to determine if the limited cell technology can be adapted to a specific application of interest. NUC has provided this type of assistance to each of the activities listed below during FY 75.

Marine Mammal Research

The Naval Undersea Center is using AA sized hermetically sealed lithium cells (similar to the heart pacemaker battery) with marine mammals to power sensors and RF transmitters that telemeter brain waves along with eye and muscle movement. The required life of the battery is 1800 hours of "on" time

and the battery consists of two cells, one AA sized delivering a positive three volts and one half sized AA cell delivering a negative three volts. Lithium inorganic cells, as compared with previously used mercury batteries, are advantageous for this application because of their high available power and long life in a compact form, their lighter weight and no gas venting. The instrumentation package is shown in Figure 26.

Balloon Instrumentation Package

The Naval Undersea Center is using 25 double D-sized hermetically sealed cells for each balloon supported radio package. Two power levels are required from the battery, 16 volts at 150 milliamperes and 13 volts at 800 milliamperes. The total operating time is 120 hours. The main advantage of lithium batteries for this application is their high energy and light weight since the battery weight is not to exceed 10 pounds. This could not be accomplished by any other type of battery. Twenty instrumentation packages will be built. The balloon to be instrumented is shown in Figure 27. Figure 28 shows the battery case and cells.

Laser Designator Power Source

The Naval Weapons Center, China Lake, CA and NUC have used high rate cells to energize a laser in a target designation system as shown in Figure 29. The requirements for the tests were to deliver 6 to 10 amperes in a pulsed mode (one minute on and one minute off) at a voltage greater than 20 volts. A test was made to compare the number of pulses available from a series circuit of ten high power lithium inorganic cells against the standard NiCd battery pack. The

Figure 26. Biotelemetry Package Using AA Size Lithium Cells



Figure 27. Tethered Balloon System Using 25 "D" Size Lithium Cells



Figure 28. Battery Container for Tethered Balloon Systems



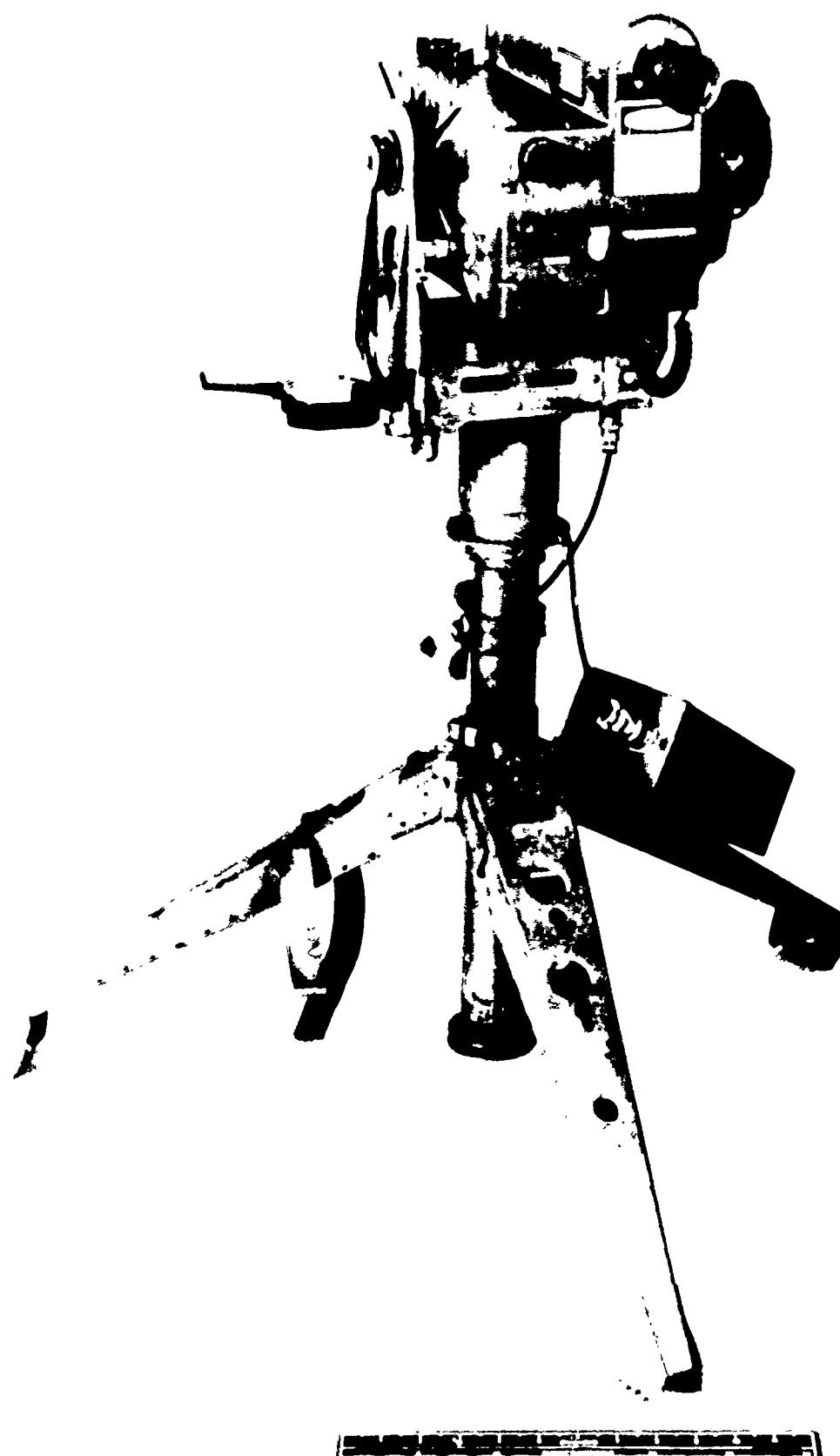


Figure 29. Modular Universal Laser Equipment Using 10 "D" Size Cells

lithium battery pack delivered 50 satisfactory cycles whereas the NiCd pack delivered ten cycles. Additional development is planned for FY 76 to optimize high rate cell design for this application.

Deep Ocean Transponders

Several transponders (shown in Figure 30) developed by Sonatech, Inc. Goleta, CA will be installed in the ocean with lithium inorganic electrolyte batteries. The battery pack has two requirements, a low level receiver and a high level transmitter. The low level receiver requires 8 volts and a continuous 1 milliampere for a period between six months and five years. The high level 200 watt transmitter produces 10 millisecond pulses at 24 volts for 2 million pulses over a five year period. The battery pack consists of 40 D-size cells, however, the double D-size cell is being evaluated for this application.

Geophysical Monitoring Balloon

A lightweight, expendable command receiver has been developed at UCSD for ONR for terminating scientific balloon flights as shown in Figure 31. The receiver operates at 138.54 MHz and the command is actuated by a sliding tone from 300 Hz to 400 Hz. A Phase Locked Loop detector circuit operates an SCR fixing circuit to actuate a guillotine type explosive cutter. Experience with the command receiver has shown that most high energy density batteries freeze-up at high altitudes and provide insufficient current to fire the squib. It is believed that the lithium inorganic electrolyte battery will be less likely to freeze at the high altitudes anticipated in most balloon flights (freezing point for thionyl chloride is -104.5°C). Test flights are planned in FY 76 to determine the command receivers performance with a 15 volt lithium inorganic electrolyte battery.

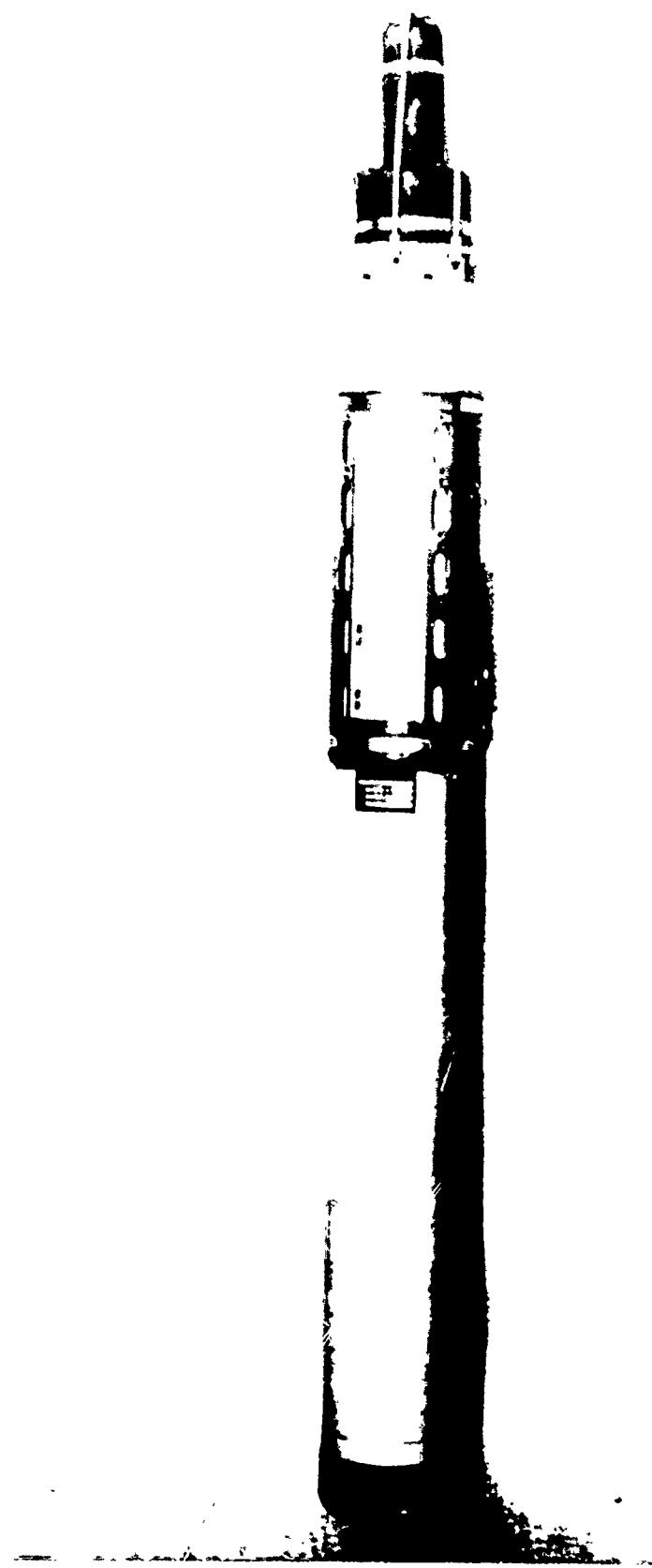


Figure 30. Deep Ocean Transponder Using 40 "D" Size Cells

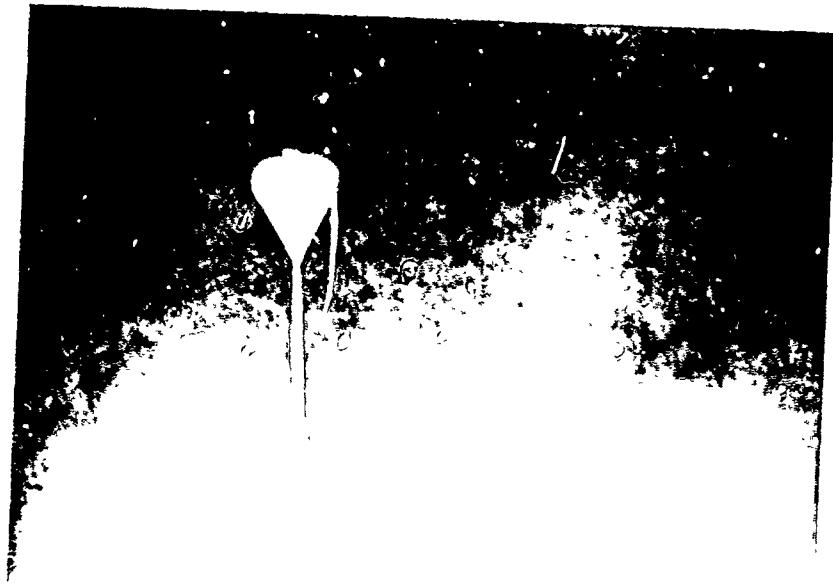


Figure 31. Geophysical Research Balloon Using 5 "DD" Size Cells

NAVFAC Lightweight Cable Experiment

The NUC, Hawaii Laboratory is constructing an underwater cable system experiment. Five battery packs are needed for a central electronics battle, two sound velocimeters and two current meters. The system will be deployed for a year in the deep ocean with an ambient temperature near 0°C. The system, except for the acoustic receiver, will be off until it is interrogated by an acoustic command. The acoustic receiver will be energized for the entire one year system life. The system will be interrogated every hour for a year and will be on for three minutes for each interrogation.

Since power source space, weight and reliability are critical in this application 50-size DD and 25-size AA lithium inorganic electrolyte cells will be used.

The batteries are to be in a sealed container for a year with the electronic circuitry they are powering. Therefore, they should not leak any gasses or liquids that will cause corrosion or short circuiting of the electronics. For this reason only hermetically sealed cells will be used.

Arctic Data Buoys

Polar Research Laboratory, Inc. (PRL), Santa Barbara, CA is developing under NOAA contract an air droppable (ADRAMS) data buoy for use with the NUMBUS F satellite. This is similar to the NUMBUS F data buoy work performed for ONR. PRL is also developing a different type of arctic data buoy for Sensor Technology Program (ONR) that could well utilize lithium inorganic batteries.

The first application at PRL will be the ADRAMS (shown in Figure 32) because the inorganic lithium battery appears to solve several of the problems that have been experienced with other power sources. The requirement is 175 amp-hours at



Figure 32. Arctic Data Buoy

12 volts with peak loads of 250 ma for 1 second each minute. Hermetically sealed "DD" size cells are being used for this application.

The experience gained from this initial arctic application will provide engineering data for the other similar applications that need an advanced power source. Laboratory tests conducted by PRL have shown an ability to pulse discharge double "D" size cells for 1 second per minute. The following data has been obtained at 66 ma:

| <u>Temp (°C)</u> | <u>Starting Voltage</u> | <u>Voltage at End of 1 Sec</u> |
|------------------|-------------------------|--------------------------------|
| -40 | 3.6 volts | not measured |
| -62 | 3.6 volts | 3.2 |
| -68 | 3.53 volts | 3.0 |

The same cell has provided 20 Ah above the cutoff voltage of 3.0 volts at a discharge rate of ~28 ma and at -15.7°C.

Seismic Sensors

The U.S. Geological Survey will be installing several sensors in the Santa Barbara Channel this year to monitor seismic activity around the Dosquadros Oil Field. These sensors require a five-year, reliable power source with a highly regulated output (1%) since they will be supplying power to voltage controlled oscillator (VCO) circuits.

Hermetically sealed DD size cells will be used for this application.

All of these applications are now using lithium-inorganic electrolyte cells but with technology improvements accomplished during FY 75. These accomplishments include hermetic seals, larger cell sizes, depassivation techniques, shock and vibration limit information, disposal methods, causes of explosions and methods of eliminating explosions.

There are many additional applications that require an advanced power source that could be satisfied by lithium inorganic cells if development for these applications was carried out. A partial list of known applications is given below:

| <u>Activity</u> | <u>System</u> | <u>Cell Size</u> | <u>Cell Rate</u> |
|--|-------------------------------|------------------|------------------|
| Naval Electronics Systems Command, GE, Sanders | Moored Surveillance Systems | 1000 AH | Low |
| Naval Undersea Center | Countermeasure (MOSS) | 160 AH | High |
| Naval Undersea Center | Advanced Lightweight Torpedo | 50 AH | High |
| Naval Air Systems Command | Sonobuoy (DICASS) | 10 AH | High |
| Naval Air Development Ctr | Countermeasure (ADDS) | 20 AH | High |
| Naval Air Development Ctr | Sonar Devices (ERAPS) | 20 AH | High |
| Naval Research Laboratory | Search Vehicle | 10,000 AH | Low |
| Naval Undersea Center | Vehicle (STARS) | 10,000 AH | Low |
| Naval Sea Systems Command | Submarine Targets | 100 AH | High |
| United States Coast Guard | Aids to Navigation Buoys | 2000 AH | Low |
| U.S. Marine Corps and U.S. Army | Field Radios | 10 AH | High |
| Naval Sea Systems Command | Swimmer Delivery Vehicles | 1000 AH | High |
| Naval Electronics Lab Ctr and Naval Weapons Center | Night Vision & Portable Radar | 10 AH | High |

Appendix B describes a computer program that was prepared to perform cost, weight and volume trade-off analyses for various hypothetical applications. Individual cases (224) were computed for twenty power-source candidates (various batteries, thermoelectric generators, solar cells, engine generators, etc.), based on a matrix of hypothetical application requirements involving various operating depths, power levels, and operating durations. The results of this analysis provide a comprehensive comparison of size, weight and cost data.

among the power source candidates. This data now facilitates the identification of applications that could benefit by the use of these lithium cells.

In summary the chemistry of the lithium-inorganic cell works and produces a battery with outstanding performance. There is a definite need for this cell in both high rate applications (i.e., vehicle propulsion systems) and long term, low rate applications as in surveillance system power sources.

CONCLUSIONS

As a result of the FY 75 development effort the following conclusions have been reached:

- The chemistry of the lithium-inorganic cell works and produces a battery with outstanding performance.
- The advantages of using lithium-inorganic electrolyte cells are numerous:
 1. High energy density (200-250 WH/LB)
 2. High cell voltage (3.6 VDC)
 3. Potentially long shelf life
 4. Long operating life
 5. Completely contained and no moving parts, fluids or gases
 6. Atmospheric pressure internally
 7. Good low temperature performance
 8. Good voltage regulation
 9. Potentially least expensive in larger size cells
 10. Wide range of sizes possible
 11. Can be pressure equalized for deep ocean applications
 12. Good tolerance to high shock and vibration

The eleventh has a tremendous value when larger batteries are to be used at deep ocean depths of 20,000 feet. Massive pressure hulls to house the batteries can be eliminated by pressure equalizing the cells.

- There is a definite need for this cell in both high rate applications (i.e., vehicle propulsion systems) and long term, low rate applications as in surveillance system power sources.
- The Fiscal Year 1975 effort has demonstrated the capabilities of the cell as well as uncovered some of its limitations. Basic work is

still needed to understand the causes of these limitations and to suggest ways to minimize or eliminate them.

- Future development work needs to concentrate on six of these problems:
 1. cell detonation following puncture
 2. the "sleeping" phenomenon
 3. voltage delay following storage
 4. dendrite formation
 5. high power density applications
 6. large size cells
- The accomplishments resulting from this program are summarized as follows:
 1. Numerous applications have been investigated, consultation has been provided to potential users including performance demonstration tests and lithium-inorganic electrolyte batteries are now being used in several applications.
 2. Required cell design improvements have been identified.
 3. Improvements in cell design have been accomplished
 - Orientation for full capacity
 - Non-attitude sensitive design
 - Chemical additive for stable cells at high temperature
 - Pressure equalized cell design for deep ocean
 - Larger cell design, fabrication and test (>100 AH)
 - Low-cost, non-leaking cell seal
 - Methods of eliminating initial voltage delay
 - Non-corroding case
 - Reliable solder tabs

RECOMMENDED DEVELOPMENT

A future development program should fully explore the major problem areas that currently bar general fleet use of the lithium inorganic cells.

The goal of this program should be to solve these major problems and assist in the initial application engineering work needed for projecting the technology toward wide scale use in the Navy.

The major problems that should be addressed under a development program are:

1. Explosion caused by cell puncture
2. Cell "sleeping" effect
3. Voltage delay and passivation
4. Dendrite formation
5. High power density cells
6. Large size cells

The nature of these problems and the proposed investigations are presented in the following discussions.

Puncture Tests

1. Thin filaments of lithium will be placed in a glass ampule containing a thionylchloride sulfur suspension. Known amounts of current will be sent through these filaments until they melt and react with the sulfur. This is an attempt at duplicating the suspected reaction that ignites the thermite-like reaction.

2. A matrix of puncture tests will be conducted aimed at determining the reason for the explosion. This includes altering the material used in the penetrating object and altering the load current in the cell.

3. Varying amounts of S_2Cl_2 will be incorporated in the high power cells to determine its effectiveness as an explosion preventative.

4. The energy liberated by the explosion will be determined.

Cell Sleeping

1. Isolate several hermetically sealed cells and monitor the voltage of the cells as they discharge. Some cells will contain the sulfur monochloride additive. This will determine if the normal pressure produced in the cell is sufficient to force the electrolyte into the electrode gap.

Voltage Delay

1. Subject the surface of the lithium to neutron activation to determine the presence of a transition metal or any other metal capable of activation analysis.

2. A program of discharging cells after a predetermined period of passivation will be started. Once each month a hermetically sealed AA sized cell will be connected to a load and the voltage rise during depassivation and total ampere hours available (as a function of storage time) will be monitored over a one year period.

Dendrite Formation

1. A glass cell will be built in order to observe the growth of dendrites.

2. Methods of preventing a reverse or charging current in multicell applications will be determined.

High Power Density Cells

1. High Power Density Cells will be designed and constructed utilizing different techniques to increase their performance.

Large Size Cells

1. Develop and test experimental and prototype cells with capacity of 1000 to 10,000 ampere hours for discharge rates of 2 weeks, 1 months and 1 year.

REFERENCES

1. Auborn, J. J., et. al., "Lithium Anode Cells Operating at Room Temperature in Inorganic Electrolytic Solutions," Journal of Electrochemical Society, 1613-1618, Dec 1973.
2. "Lithium Primary Cells: Serendipitous Search for a New Laser Leads to an Advanced Battery," Science, Vol. 184, May 1974.
3. Marincic, N., Epstrin, J., Goebel, F., "Performance of Lithium Batteries with Organic and Inorganic Solvents," GTE Labs Inc., Jan 1974.

APPENDIX A

100 Ah Lithium/SOCl₂ Cell

Prototype Construction for
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Introduction

Various electrochemical systems have been tried in the last several years in building lithium batteries. Most of the prototype cells made so far were of the wound electrode type, with a close spacing and the large surface area electrodes. This was necessary, because of a relatively low conductivity of electrolytes used in building lithium cells,^{and they} normally would not be able to deliver their energy at high rates.

There is a wide area of application, however, where the high rate of discharge is not required. A better utilization of the cell space and higher energy densities would be possible to achieve if these cells were designed without this high discharge rate in mind. A study has been conducted at GTE Laboratories of the interdependence of various factors determining the performance of such cells. The report enclosed (1) contains the details of the study and describes the optimized cell design for the low discharge rate application.

Discrepancies may be expected between the projected and the realized cell performance, when one begins to scale up the cell. An assumption was made in those studies that the porous cathode structure absorbs and holds the electrolyte at any stage of discharge. This was found to be true for small cells but may not hold for larger cells and different diameter/height ratios. The scale up from 12 Ah (D size) to 100 Ah single cell capacity seemed like a good opportunity to test the applicability of the design to larger cells.

Cell construction

With the funding for the work limited to a minimum, the prototype cells had to be made with no tooling involved. The cell can was selected from the available stock as closely as possible to the size of the single cell required. The can dimensions were:

2.797" O.D.

2.735" I.D.

4.641" High

The can material was cold rolled steel. A demountable structure had to be used to hold together the cell components. The figure enclosed represents the structure design proposed. Fig. 1. The structure had to be modified for reasons of simplicity, but the cell dimensional characteristics were not affected.

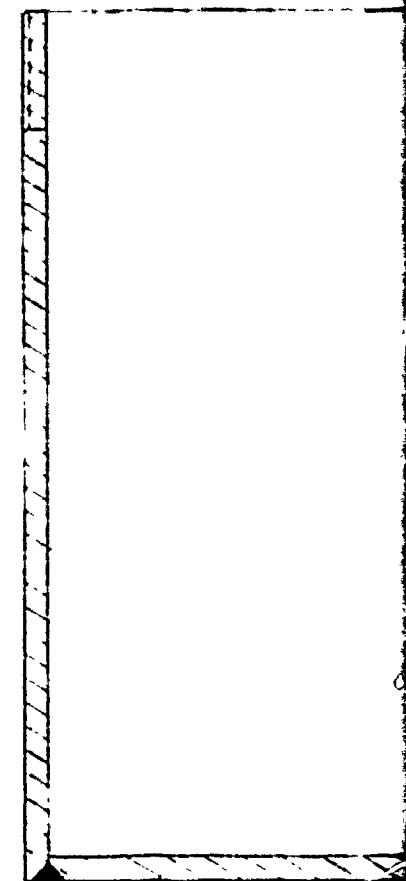
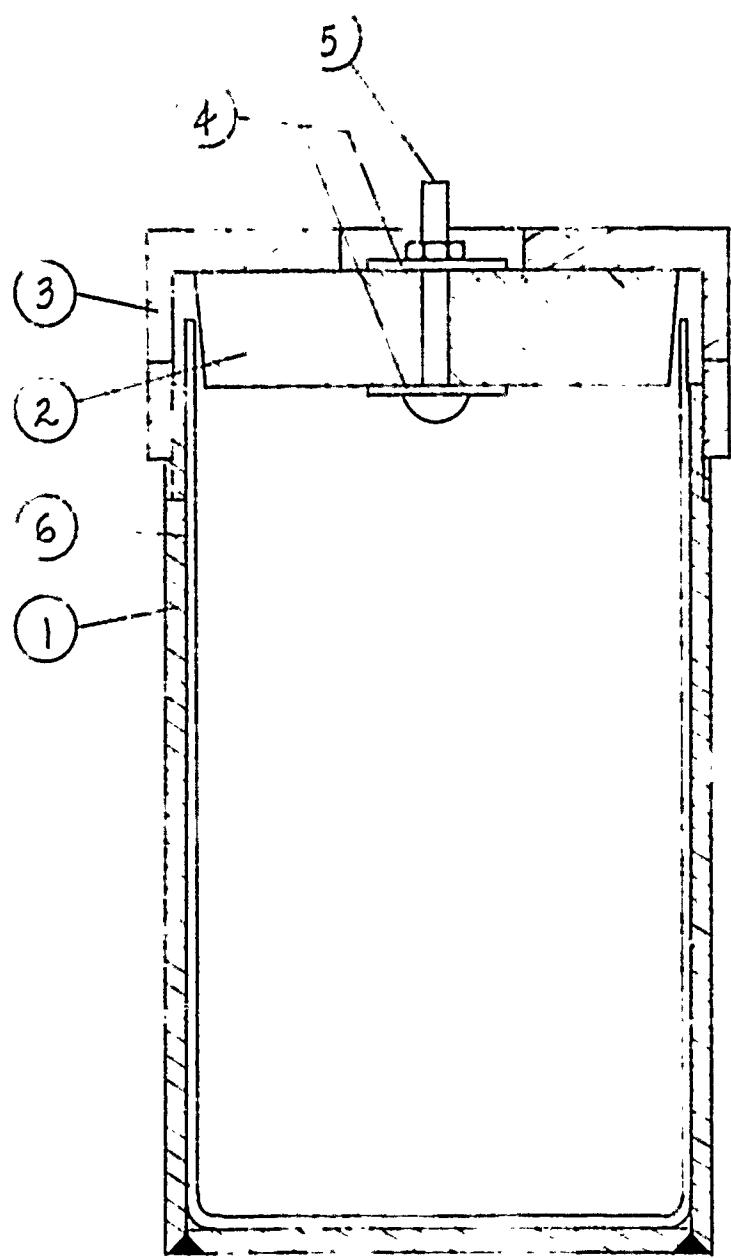
The design procedures described in the study report have been applied in the construction of the cell. The calculation showed that the cell should be able to deliver as much as 150 Ah, under extreme low rate of discharge. It must be remembered that this design has not been tested before and, therefore, the upper limit of the discharge rate has not been established. It is believed, however that a continuous discharge with approximately 50 mA will last over 3 months (50 mA for 3 months amounts to 108 Ah). The cell performance is not expected to depend much on the discharge temperature between, say, -20° and 40° C.

Preliminary test results.

One cell was made, identical in construction to those delivered to NUC, for testing in our laboratories. The projected time of discharge was shortened by increasing the discharge rate in order to obtain sooner some preliminary performance figures. The cell was placed on discharge through a constant load of 12 Ohms. As of this date, the cell delivered 45 Ah at an almost constant voltage of 3.45V. The discharge current of 287 mA may be too high for this cell construction, since the cell voltage showed a tendency to decrease. The discharge rate will be reduced to the figure corresponding to the 3 month rate, for the remainder of the cell life in order to establish the remaining deliverable cell capacity. A partial cell discharge is shown in Fig. 2.

Preliminary Experience

The cell construction appears to be feasible. The fabrication of the prototype components proceeded as planned with no major difficulties experienced. The tooling could be developed on the basis of this preliminary experience, speeding up the assemblage to a rate at which the cells may be produced at reasonable costs. However, the tooling should be preceded with the design evaluation of cell components within demountable structure since a choice of cell dimensions exists within the same total cell volume.



MATERIAL

(1) 304 SS

(2) TEFILON

(3) 304 SS

ϕD^*

2.810 $T \pm 0.010$

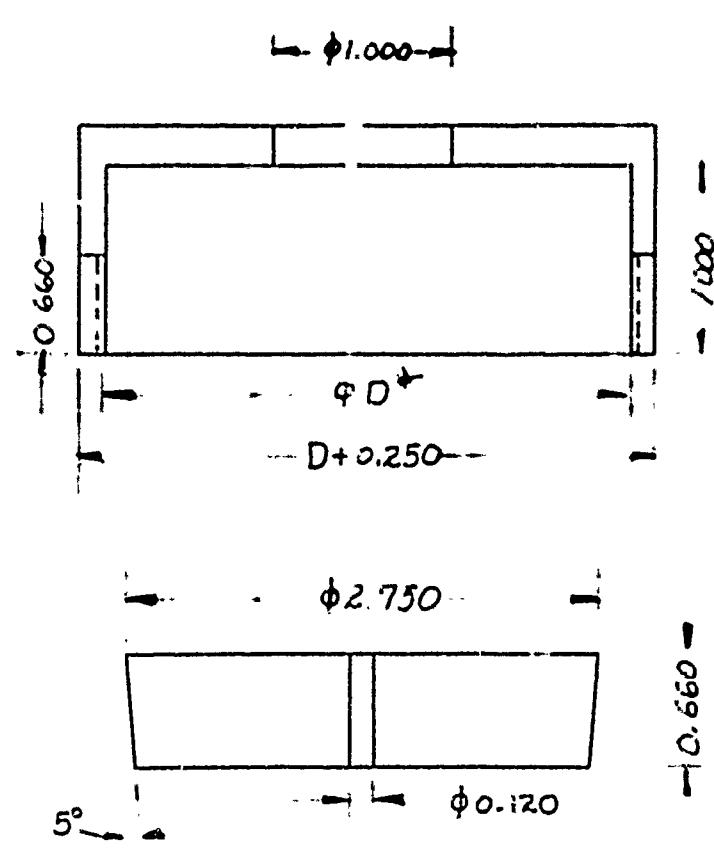
→ 0.660 ←

- 0.010
- 0.200

1

- 4.135

- 4.200



100 Ar DEMOUNTABLE CELL

FULL SCALE - DIMENSIONS IN INCHES

FIGURE 1.
Page 88

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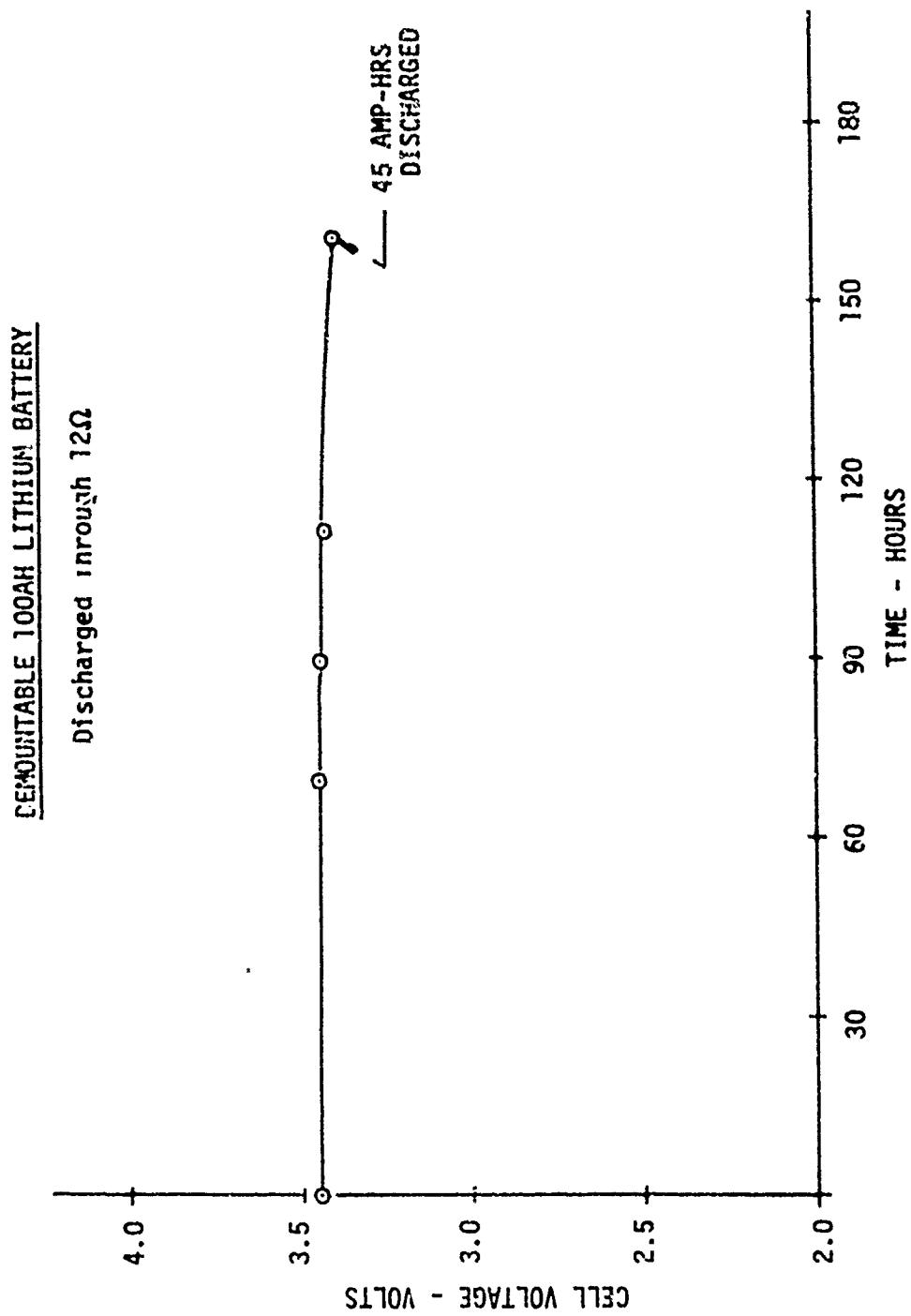


Figure 2.

APPENDIX B

SELECTION OF POWER SOURCES FOR REMOTE OCEAN ORIENTED APPLICATIONS

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Abstract

The purpose of this paper is to aid mission planners and design engineers in choosing the best available power system to satisfy the power requirements for a particular mission. It provides an overview of electric power supplies suitable for remote applications. Particularly, emphasis is placed on power supplies for missions requiring low average power and long life. Included are radioisotope power generators, sealed chemical batteries, seawater batteries, transmission cables, fuel cells, gas-fired thermoelectric generators, solar batteries and wind generators. This data will permit the user to quickly identify the power system, in the existing inventory, which will satisfy the minimum mission requirements or that which can be most economically modified to meet these requirements. In addition, the power supply category which best lends itself to the design and development of a new power system is easily identified.

Introduction

In order to realize the greatest probability of success in a mission, the power supply must be considered at an early stage and integrated into the system design. Power supply selection is controlled by such mission requirements as power level, life time, reliability, site location, ambient temperature and pressure. It is usually desirable to minimize size, weight and cost, within the constraints of the mission objectives.

This paper provides data concerning proven electrical power systems that are presently available for use in ocean oriented missions. It is intended to aid mission planners and design engineers in choosing the best available power system to satisfy the power requirements for a particular mission. In addition, it provides an overview of electric power supplies suitable for remote applications. Particularly, emphasis is placed on power supplies for missions requiring low average power and long life. Included are radioisotope power generators, sealed chemical batteries, seawater

batteries, transmission cables, fuel cells, gas-fired thermoelectric generators, solar batteries and wind generators.

Data is provided to allow comparison of candidate power supplies based on cost, size, weight, power, life and other mission requirements. Parametric data was generated using a computer for hundreds of cases of mission time, power level and location (i.e., ocean surface to 20,000 ft depth). The data presented is based on the best published technical information available, laboratory tests, ocean tests and personal visits or telephone conversations with qualified sources.

Study Constraints

A broad survey was made of known power sources. The survey addressed (1) power sources that are available as off-the-shelf products or only require engineering for a specific application and (2) feasible power sources under development that will be available in the near future that offer significant advantages over currently available sources in terms of endurance, energy density, cost savings or ease of deployment. Also of particular interest are power sources that do not require or minimize the use of atomic energy sources, critical materials such as silver and platinum, potential pollutants such as mercury and long (hundreds/thousands of miles) cables containing tons of valuable copper conductor, steel and polyethylene. Power sources whose development is well in the future or uncertain, as nuclear fusion or which are not appropriate to our application, as manpower or marine mammals, are not included.

Information was obtained through literature surveys and personal interviews. Literature sources included government agency and private company reports, patent files, open technical literature and other sources. The Navy has previously conducted programs of a similar nature. This information is repeated only where necessary for reporting continuity.

The data analysis was bounded by the following conditions regarding missions and systems of interest:

- a. Electrical power is the desired form of energy output and various hydraulic, pneumatic or mechanical transmission systems are not considered.
- b. Anticipated performance is projected 3 years into the future. Consequently, analysis includes promising theoretical developments as well as current experimental components. The period beyond 3 years is not extensively explored.
- c. System power levels lie roughly between one watt and 1000 watts and a constant electrical load is assumed.
- d. Load durations are greater than one hour; however, some consideration is given to storage systems which can be applied for short term peak load application.

A tremendous number of devices and physical phenomena appear useful in ocean power systems, as shown in Figure 1. A wide variety of systems - mechanical, thermal, chemical, electrical, radiant and atomic - will be required to satisfy the complexity and scope of anticipated future missions. It appears impossible at this time to eliminate any of the major types of power systems under consideration as each will eventually find a niche in the power-level, mission-duration continuum where it appears most useful.

Basic Power System Methods

There are only three basic methods which can be utilized for supplying electrical power to ocean systems. It can be used or transmitted from a power generator located on or near the surface or generated by a power source located adjacent to or integrally with an undersea system. The ability to supply the required power by these methods should be established early in a program so that system designs and site selection can be based on military, political, scientific and economic needs without constraint from the power supply.

The primary consideration in the design of most long life ocean oriented electronic systems is reliability. Redundant generation and transmission systems should be provided wherever possible to preclude termination of an operation because of a single power equipment failure. Some missions will also require emergency power sources with sufficient power and energy to insure system operation until repairs are completed.

General concept designs for the three fundamental methods of supplying power were prepared so that an identification of the necessary technology could be made. These concepts are discussed below.

Transmission from Shore Stations

Generation, transmission and distribution of electrical power on land is a mature industry wherein the selection of equipment and systems designs are dominated primarily by economic considerations. Essentially, any quantity of electrical power may be obtained from public utilities or from transportable engine-generators. Fuel logistics for remote site operation is well established and an adequate quantity of power can therefore be assumed to be easily obtained at most shore stations of interest to the U. S. Navy.

A high voltage cable laid on the seafloor could supply power from shore to the undersea system. Multiplexed data can be transmitted on the power cable and this is commonly practiced in utility and ocean communication systems. Although numerous concepts could be made, they would employ the same basic equipment and manifest the same technical problems and essentially the same technological maturity.

In this concept the undersea cable would be entrenched into the seafloor to a depth sufficient to escape influence of wave and tidal action. Each cable would be laid separately to minimize the probability of simultaneous damage by trawlers or other seafloor activities. Practicality of this method is determined primarily by the economics associated with cable system fabrication and installation.

Transmission of Power from Surface Platforms

Energy storage and the transmission of electrical power from surface platforms to seafloor facilities is similar in concept to transmission from shore stations. For high power requirements conventional air breathing engine-powered generators are commercially available. Station keeping ships or barges can be used for short duration missions or missions which otherwise require their presence. For longer durations, where technical factors or economics preclude surface ship use, the power source could be installed in a surface or spar type buoy with refueling or battery recharging performed at periodic intervals. An alternate approach would be to install an energy storage source in or adjacent to the undersea system with an umbilical to the surface through which recharging can be accomplished.

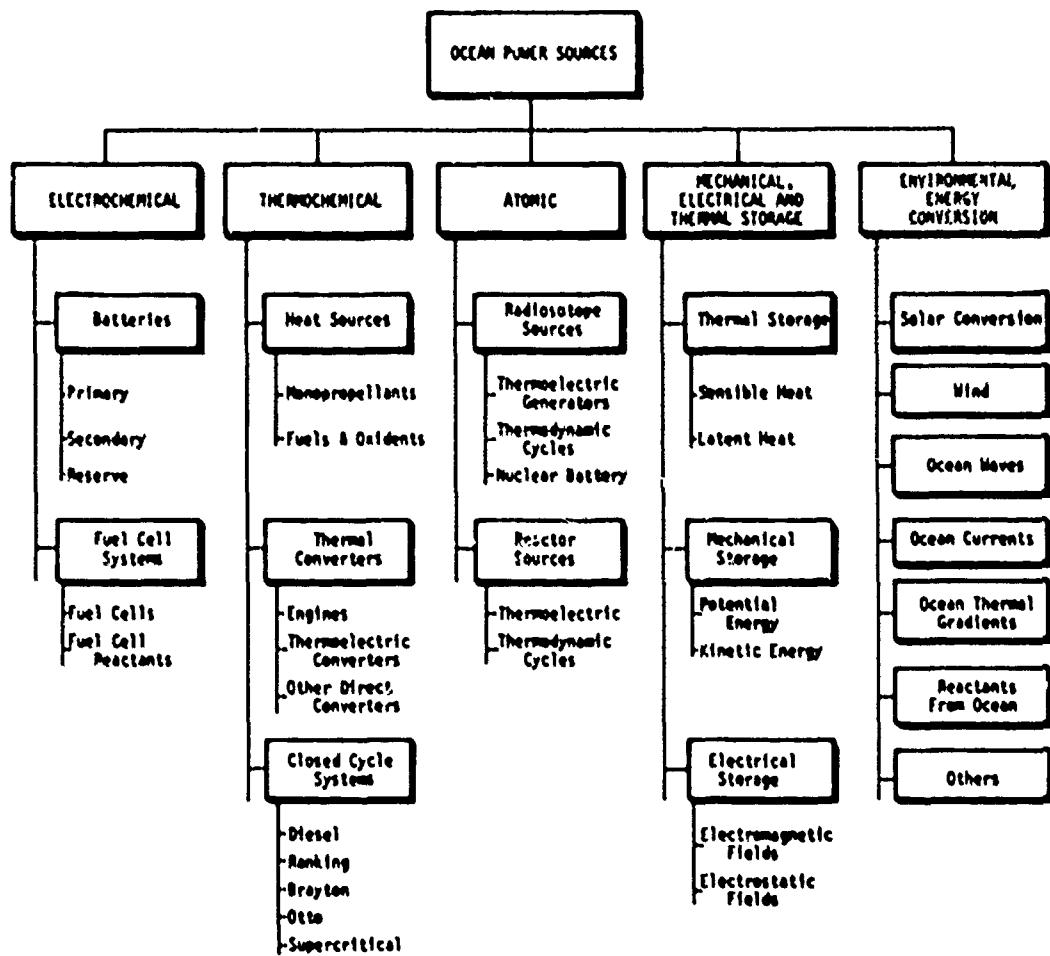


Figure 1. Structure of Power Source Technology

Power Generation In Situ

Generation of electrical power in situ is severely limited by the absence of naturally occurring chemicals which can be combined to recover energy either electrochemically or through combustion processes. Naturally occurring heat sources are limited to low temperature gradients found in the ocean column and to the earth's interior which could possibly be tapped to provide geothermal heat. For the most part, however, only chemical and atomic systems are within near term advanced technology realization. Economic, safety and administrative considerations often preclude the use of atomic power except for critical, long mission duration systems. There are several practical electrochemical and thermochemical in situ energy/power systems that convert the energy of stored chemicals. An atomic powered concept employs isotopic or reactor energy sources.

There is another significant variation of the sea-floor power system concept that would increase the possible operating life of an electronic system to ten or more years. This concept involves rechargeable, refuelable or replaceable energy storage devices. Manned or cable controlled submersible systems equipped with manipulators could be used to replace the expiring sources. Underwater mateable mechanical or electromagnetic connectors would be used to couple the power source to the electronic load. Similarly, battery modules or reactant tanks could be replaced at intervals to increase the life and reliability of the system.

Survey of Power Sources

A power source consists typically of an energy conversion system for converting the stored energy into a form usable for the desired application; the power source may or may not also include the energy source depending on whether the stored

energy is furnished with the energy conversion system, either integrally as in a battery or separately as in the fuel for a heat engine, or whether stored energy is extracted from the environment, for example, chemical energy by an air breathing heat engine or kinetic energy by a windmill.

For most applications the desired output of the power source is electrical current. Energy conversion from the stored energy to the electrical output may be in one step, as the stored chemical energy of a battery is converted to electrical energy by galvanic action, or in two or several steps as in a diesel generator in which the stored energy of the fuel and oxidizer are converted from chemical to thermal to mechanical to electrical energy.

The high energy content of some chemical fuels makes possible the storage of energy source material for ambitious missions. The use of thermal storage is promising for short term missions where the simplicity of an available heat source is of value. The use of environmental energy sources makes possible indefinitely long endurance, but power densities are low and availability (e.g., wind or solar energy) may not be predictable. Nuclear sources offer very high energy content and long life at a penalty of high initial cost.

Highly efficient electrochemical conversion devices, such as batteries and fuel cells, make the use of the energy available in chemical reactions. Unfortunately, many of the chemical reactions which do not allow the use of relatively low energy chemical reactions which do not allow the performance of the hydrogen/oxygen fuel cell on a long-lived mission. It is important to note, however, that there are various types of lithium batteries presently being developed that have energy densities equal to fuel cell power systems. These lithium batteries are available for specific applications at a cost comparable to alkaline batteries on a dollar/watt hour basis.

Thermoelectric devices are relatively inefficient, but provide long-lived static conversion which is applicable to low power missions. The thermionic converter is more efficient than the thermoelectric, although not as yet developed. It shares the simple system design. For very high power levels, magneto-hydrodynamic (MHD) converters have promise of high conversion efficiency with high temperature heat sources, but development is still in its early stages. While photovoltaic devices are obviously limited to shore installations or surface buoys and the combination of weather and diurnal cycles, they may be applicable when low power levels are needed for very long periods.

Description of Computer Program and Data Bank

A computer program (Figure 2) has been developed to convert detailed data concerning power sources for remote ocean applications into information that is meaningful to persons who do not necessarily have extensive background in the field. The primary end use is for the preliminary selection of a cost-effective power source suitable for remote marine-oriented projects requiring up to one kilowatt for as long as 10 years.

There are 3 basic parameters which are used to define the conditions under which a power source will have to operate:

- 1) Location - depth with respect to the ocean's surface - 4 ranges considered
- 2) Average Power Level - 7 ranges considered
- 3) Duty Cycle Time - duration at the average power level - 8 ranges considered

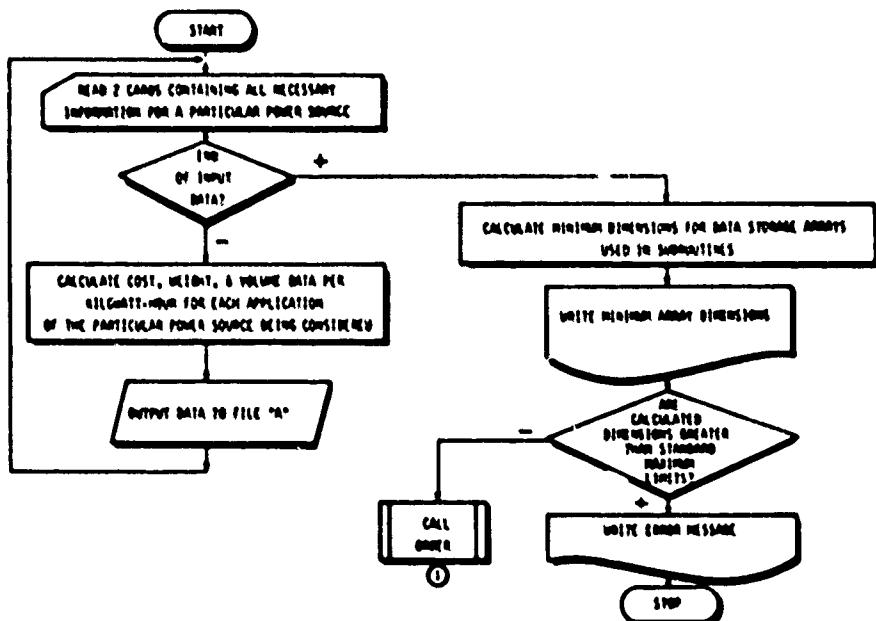
There are 224 possible combinations of the three basic parameters for which the applicability of each power source could be considered. The main program determines which combinations are applicable for a given power source, calculates cost, in-air weight, buoyant weight and volume (all values are per kilowatt hour) and associates the values with the appropriate name and comments as a single record in a temporary storage file, "A".

The first subroutine takes the output records generated by the main program and orders them according to increasing cost. This cost ordered data is stored in a temporary file, "E".

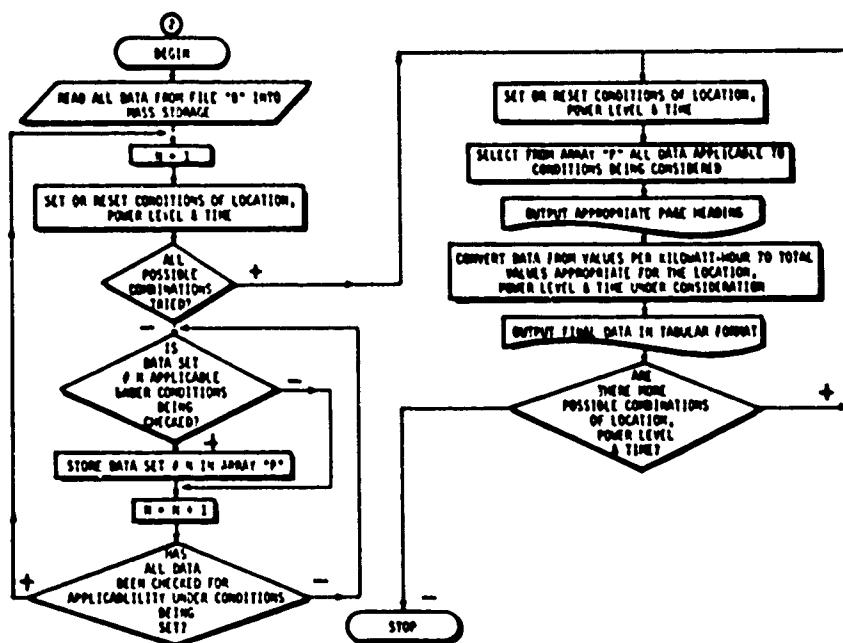
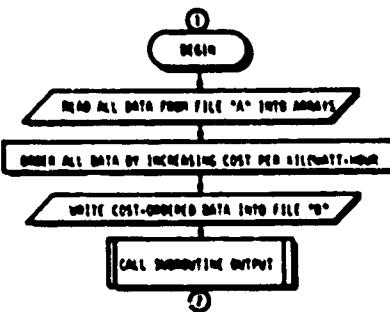
The second subroutine iterates through all the possible combinations of location, power level and time. During each individual iteration the storage file B is searched for all records applicable to the particular combination of parameters being considered and those records are retained by the subroutine. The data is converted from values per kw-hr to total values for the number of kilowatt hours for the particular case, and then listed in order of increasing cost with an appropriate page heading.

All data necessary to enter a particular power source into the program calculations is contained on two data cards which provides ease in updating the resulting output when necessary.

The primary limitation of this program is the amount of data which must be stored during program execution. The required storage allocation increases rapidly as the number of power sources considered increase. If the amount of data is to



Main Program INPUT -
 Calculates pressure vessel/containment data (in values per kilowatt-hour) for each applicable combination of location, average power level, and time for each power source to be considered.



Subroutine OUTPUT - Takes cost-ordered data from file "B" and converts values from "per kilowatt-hour" to appropriate total values for each applicable combination of location, average power level and time. The results are output in an orderly tabular format.

Figure 2. Program Flow Chart

be increased substantially, or if the program is to be executed at a facility with less than 65K words of storage, segmentation may be necessary.

Parametric Data for Power Sources

The previously described computer program was used to generate parametric data for the numerous, currently available and applicable power source candidates shown in Figure 3. Individual cases (224) were computed for the power sources candidates based on these requirements:

- 1) Locations above the sea surface, the surface to 2000 ft depth, and additional depths down to 10,000 ft and 20,000 ft
- 2) Power levels of 1/2, 1, 10, 25, 50, 100 and 1000 watts, and
- 3) Endurance periods of 1 day, 1 week,

1 month, 3 months, 6 months, 1 year, 5 years, and 10 years.

Examples of output data are given in Tables I and II.

Separate output data sheets (224) have been prepared for each case with the case number given. The power source identification number is shown in parenthesis following the name of the sources. These Identification numbers correlate with the Identification number given in Figure 3.

The output listing presents the candidates in an order of cost. Least cost power sources are listed first. Source cost, weight in air, weight in water and volume are calculated for the requirements of each particular case. The righthand column identifies critical material, hazardous materials, special limitations such as maintenance intervals and requirements for energy storage systems as commonly needed for environmental energy sources systems.

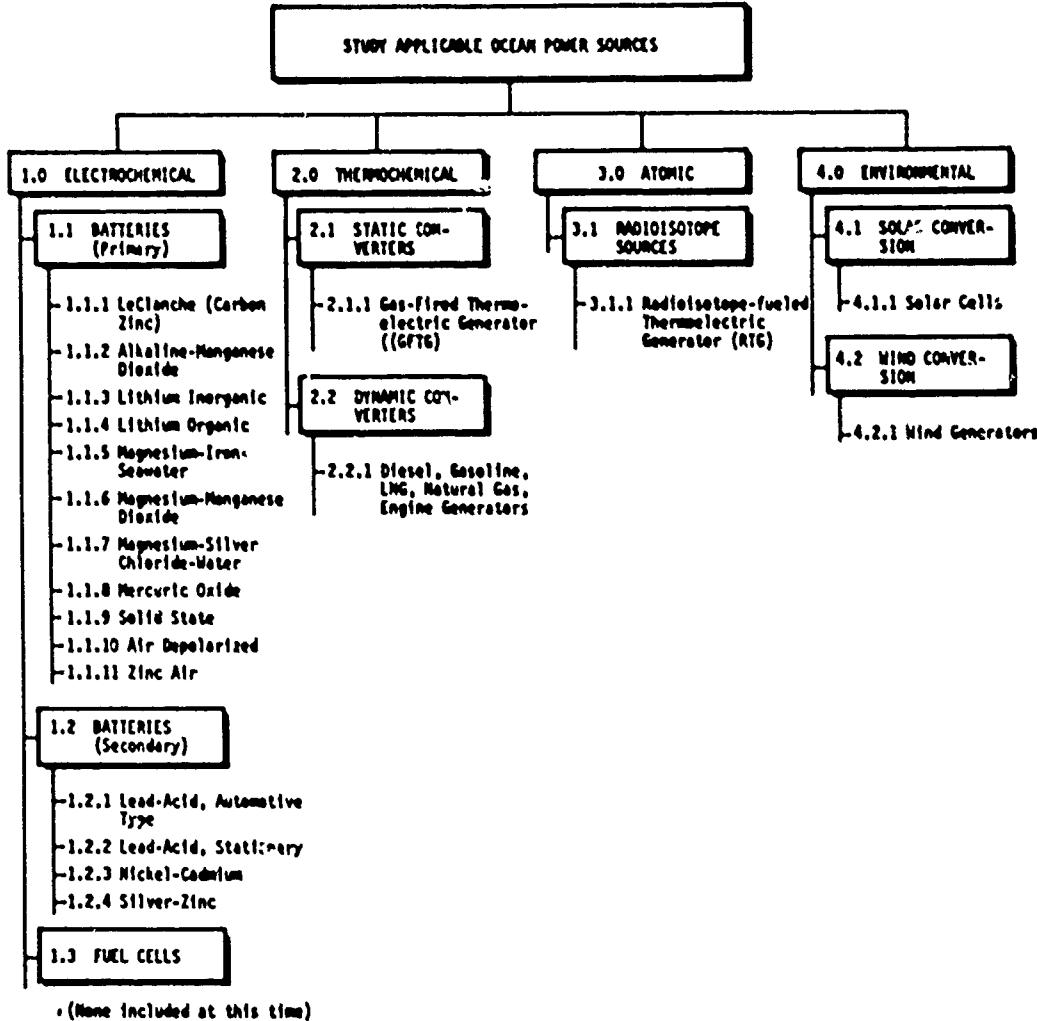


Figure 3. Study Applicable Ocean Power Sources

Table II. Example of Output Data*

| Power Source (Identification No.) | Cost (\$) | Weight (lbs) (in air) | Weight (lbs) (in water) | Volume (cu in) | Critical Materials, Etc. |
|--------------------------------------|--------------|-----------------------------|-------------------------------|-------------------|--|
| Lithium-Inorganic Cell(1.1.3) | 558 | 59 | 29 | 806 | |
| Zinc-Air Cell(1.1.11) | 748 | 159 | 70 | 2407 | Large Cell Technology High Press C2 Storage |
| Leclanche Type Cell (1.1.1) | 911 | 392 | 224 | 4525 | |
| Air Depolarized Cell(1.1.10) | 984 | 257 | 109 | 3995 | High Press C2 Storage |
| PB-Acid Stationary(1.2.2) | 1016 | 1076 | 657 | 13557 | Pressure Equalizable |
| MG-MN02 Prim Dry Cell(1.1.2) | 1117 | 244 | 122 | 3302 | |
| Magnesium-Iron Seawater (1.1.5) | 1776 | 57 | 32 | 4862 | |
| Silver-Zinc Prim Cell(1.2.4) | 5503 | 165 | 96 | 1877 | Uses Silver |
| Silver-Zinc Second Cell(1.2.4) | 6628 | 177 | 93 | 2711 | Uses Silver/Press-Equal |
| 1 Watt RTG(3.1.1) | 9167 | 5 | 4 | 22 | PU 238 Provided by ERDA |
| 1 Watt RTG(3.1.1) | 19024 | 750 | 647 | 2771 | Strontium 90 Isotope |

*Case 122. Location - down to 10,000 ft; Power Level - 1.0 Watt; Time - one year.

Table II. Example of Output Data*

| Power Source (Identification No.) | Cost (\$) | Weight (lbs) (in air) | Weight (lbs) (in water) | Volume (cu in) | Critical Materials, Etc. |
|--------------------------------------|--------------|-----------------------------|-------------------------------|-------------------|-------------------------------|
| PB-Acid Auto Type Cell(1.2.1) | 1004 | 2411 | 1319 | 35344 | |
| PB-Acid Stationary(1.2.2) | 4948 | 5345 | 3264 | 67323 | Temp Dependent Degradation |
| Lithium-Inorganic Cell(1.1.3) | 6523 | 347 | 174 | 4670 | Pressure Equalizable |
| Magnesium-Iron Seawater (1.1.5) | 8725 | 287 | 157 | 24142 | Large Cell Technology |
| Zinc-Air Cell(1.1.11) | 15105 | 931 | 435 | 13938 | High Press or Storage |
| Air Depolarized Cell(1.1.10) | 23859 | 1544 | 687 | 23136 | High Press or Storage |
| Silver-Zinc Prim Cell(1.2.4) | 36187 | 948 | 544 | 10868 | Uses Silver |
| 25 Watt RTG(3.1.1) | 70524 | 4200 | 3379 | 22167 | Strontium 90 Isotope |

*Case 181. Location - down to 20,000 ft; Power Level - 10 Watts; Time - six months.

Since only integer values are given in the printout some values of weight and volume are shown as 0. This means that the value was derived by rounding a calculated value less than 0.5. In some of the cases no power source candidates appear applicable based on the data and constraints of the program. In these cases no data sheet is printed. The cases involving power sources located above water show NA for weight in water meaning not applicable data.

Summary of Data

Since the computer output consisted of a total of 224 pages, this data was reduced and presented in summary fashion in Figures 4 through 15. The 12 data summary figures present the optimum regions of power level and endurance (operating life) for selected power sources. The power source selections are based on the criterion indicated at the top of each figure (e.g., least cost). Separate

sets of figures are provided for each application depth studied (e.g., above water, surface to 2000 ft depth, etc.).

The user of this data can quickly determine the optimum power source based only on one of these criterion. This type of summary does not provide the complete set of tradeoff data for all the parameters as is available in the computer output pages. For this purpose a report "A Guide to the Selection of Power Sources for Remote Ocean Oriented Applications", is being prepared for distribution within the Navy Department and will be available also from the Defense Documentation Center.

This report will also provide brief descriptions, special features, suggested applications and specifications for each power source candidate included in this study. This type of information can also be obtained from power source manufacturers.

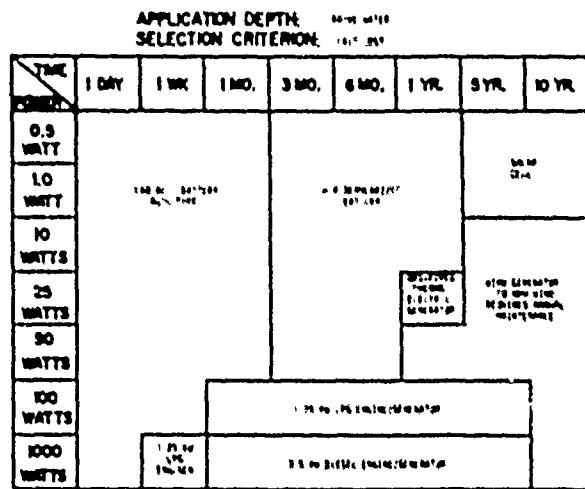


Figure 4. Data Summary

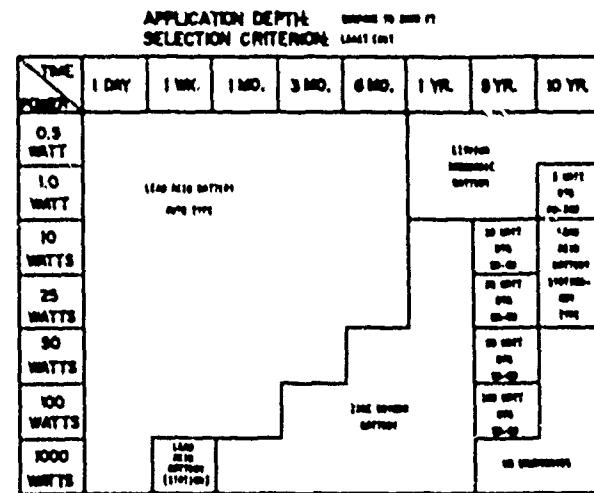


Figure 5. Data Summary

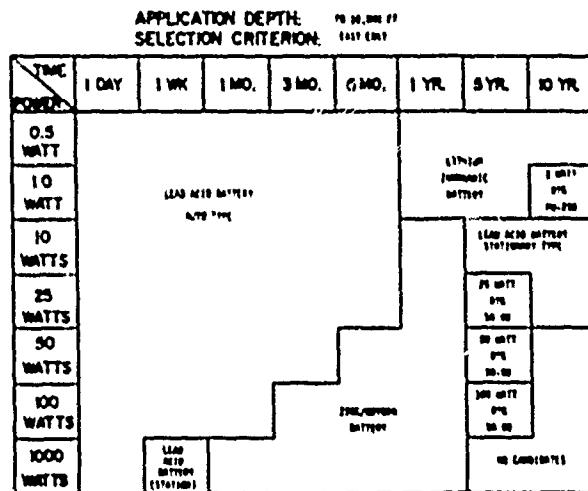


Figure 6. Data Summary

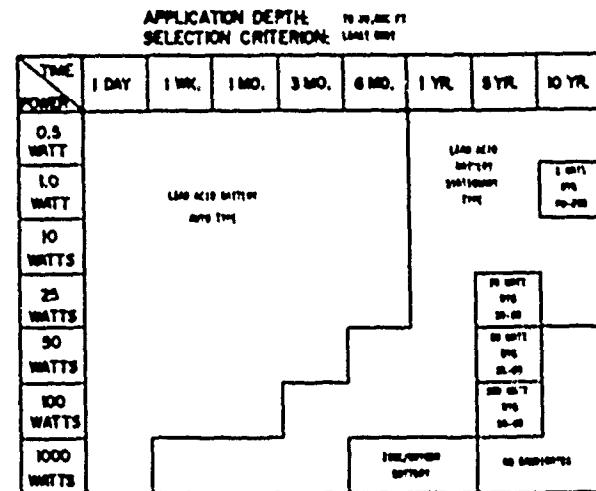


Figure 7. Data Summary

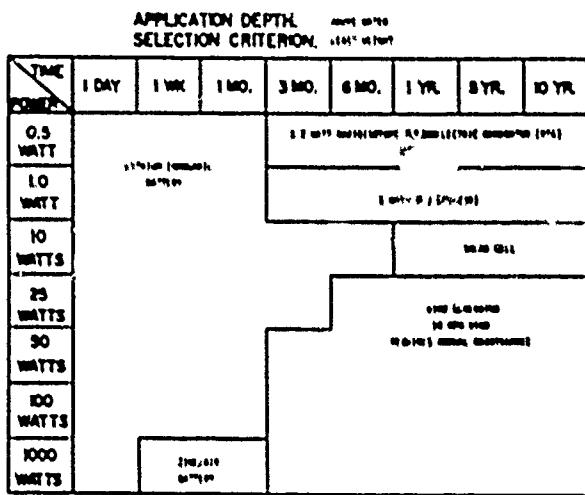


Figure 8. Data Summary

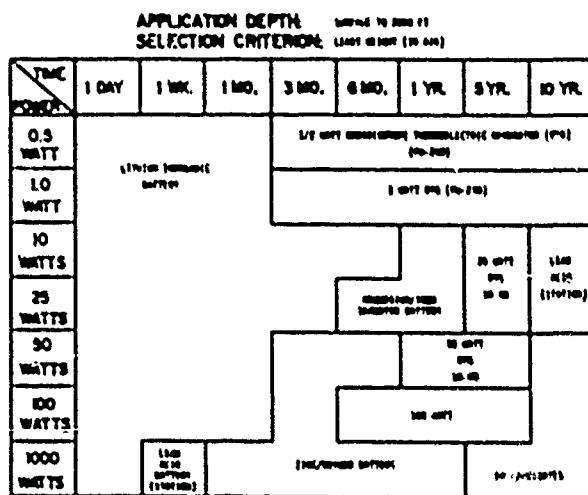


Figure 9. Data Summary

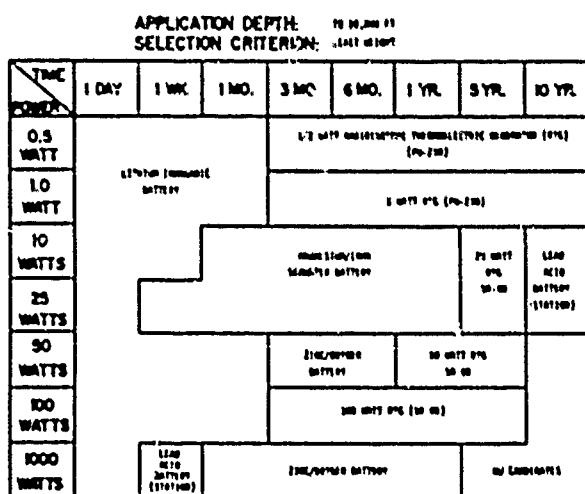


Figure 10. Data Summary

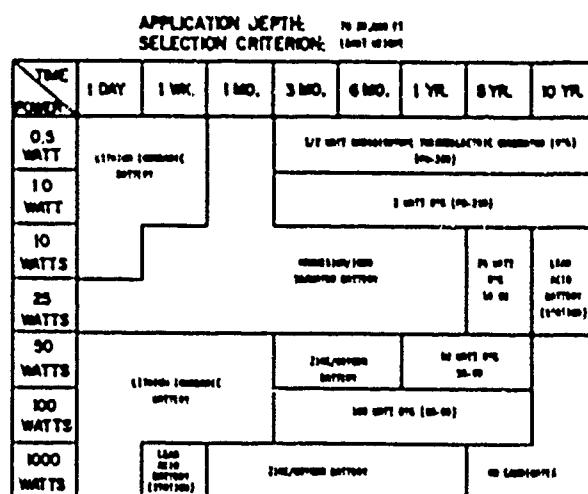


Figure 11. Data Summary

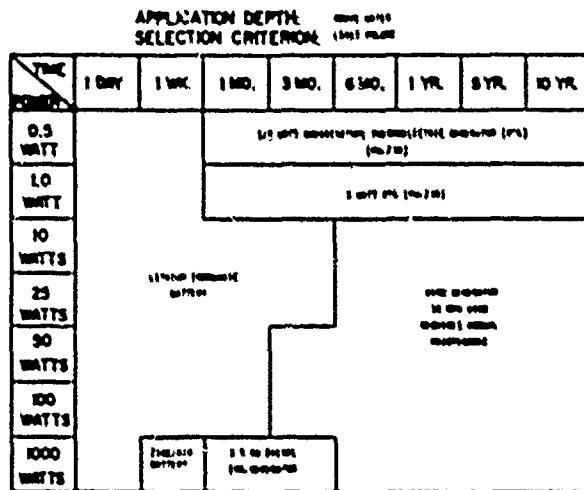


Figure 12. Data Summary

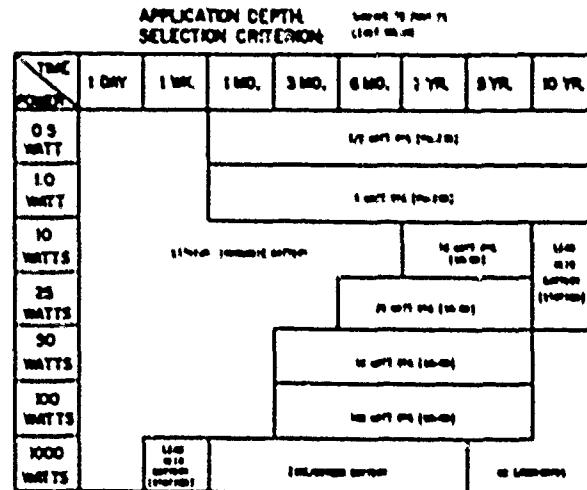


Figure 13. Data Summary

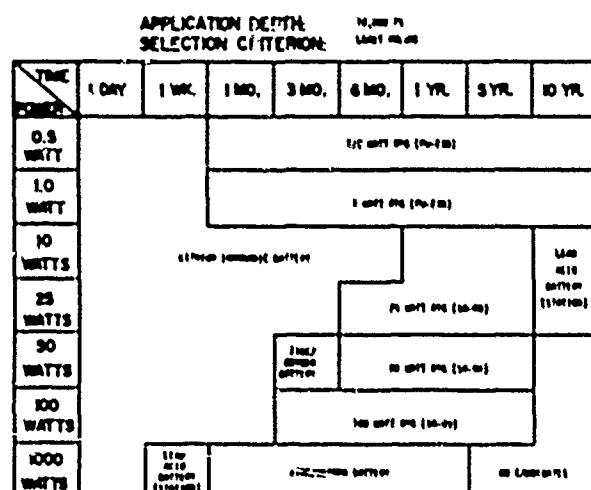


Figure 14. Data Summary

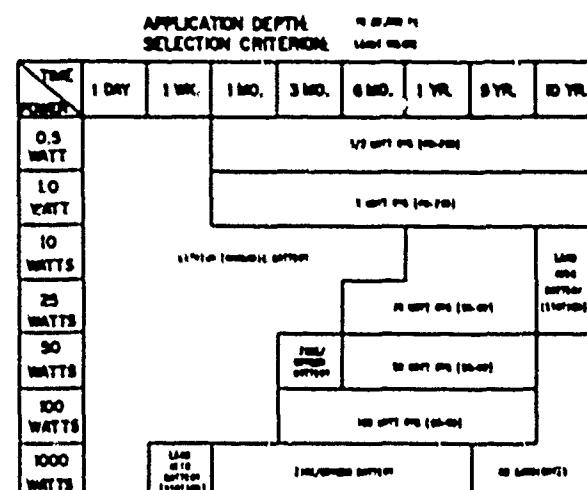


Figure 15. Data Summary

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